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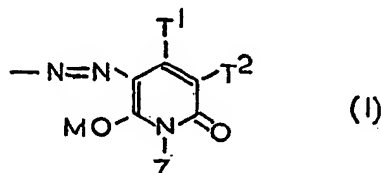
(54) REACTIVE DYESTUFFS CONTAINING 3-AZO-2-HYDROXY-6-PYRIDONE RESIDUES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to reactive dyestuffs and more particularly it relates to water-soluble azo dyestuffs containing fibre-reactive groups which are particularly valuable for colouring polyamide and cellulose textile materials.

It has been found that water-soluble compounds containing a sufficient number of sulphonic acid groups to provide water-solubility, one or more cellulose-reactive groups and at least one 3-azo-2-hydroxy-6-pyridone radical are valuable dyestuffs capable of affording deep shades of excellent fastness on cellulose, wool or polyamide textile materials.

Such dyestuffs may be characterised, for example, by the presence of at least one sulphonic acid group, at least one cellulose reactive group and at least one group of the formula:



wherein Z represents a hydrogen atom or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted,

T¹ represents a hydrogen atom, a CN, COOR¹, CONR¹R², COR¹ or OH group or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted, and R¹ and R² each independently represents a hydrogen atom, an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted or the group —NR¹R² represents the radical of a 5- or 6-membered heterocyclic ring compound,

T² represents a hydrogen atom, a CN, COOR¹, CONR¹R², or COR¹ group or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted, and M represents a hydrogen atom or a metal atom forming part of a metal-complex system in the dyestuff.

Throughout the Specification the terms "lower alkyl" and "lower alkoxy" are

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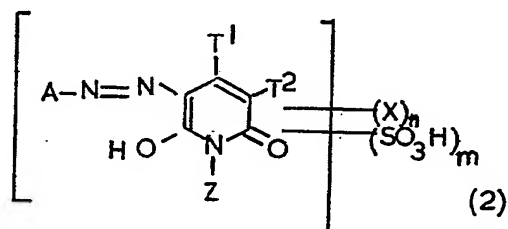
used to denote alkyl and alkoxy radicals respectively containing from 1 to 4 carbon atoms.

The optionally substituted alkyl radicals represented by Z, T¹, T², R¹ and R² are preferably optionally substituted lower alkyl radicals, and as specific examples of such radicals there may be mentioned methyl, ethyl, *n*-propyl and *n*-butyl, hydroxy lower alkyl such as β -hydroxyethyl, lower alkoxy lower alkyl such as β -(methoxy or ethoxy) ethyl, cyano-methyl, carbamoylmethyl, ethoxy carbonyl methyl and acetylmethyl.

As examples of aralkyl radicals represented by Z, T¹, T², R¹ and R² there may be mentioned benzyl and β -phenylethyl. As an example of cycloalkyl radicals represented by Z, T¹, T², R¹ and R² there may be mentioned cyclohexyl. The optionally substituted aryl radicals represented by Z, T¹, T², R¹ and R² are preferably optionally substituted phenyl radicals and as specific examples of such radicals there may be mentioned phenyl, tolyl, chlorophenyl, carboxyphenyl, methoxyphenyl and sulphonyl. The optionally substituted heterocyclic radicals represented by Z, T¹, T², R¹ and R² are preferably optionally substituted 5- and 6-membered heterocyclic rings, and as specific examples of such radicals there may be mentioned 2-pyridyl, 2-thiazolyl, 1-piperidinyl and 1-morpholinyl.

As examples of 5- and 6-membered nitrogen-containing heterocyclic rings formed by joining R¹, R² and the nitrogen atom there may be mentioned piperidine, morpholine, piperazine and pyrrolidine.

One class of water-soluble azo dyestuffs of the invention are monoazo dyes represented by the formula:



wherein A represents a benzene or naphthalene nucleus,

X is a fibre-reactive group;

Z, T¹ and T² have the meanings stated above,

n is a positive integer of at least 1; and *m* is a positive integer of at least 1.

The azo dyestuffs of the invention can exist in a number of tautomeric forms; for convenience the dyestuffs have only been formulated in one of these tautomeric forms, but it is to be understood that this Specification relates to dyestuffs in any of the possible tautomeric forms.

The radical represented by A is a naphthalene nucleus or a benzene nucleus preferably carrying at least one sulphonic acid or carboxylic acid and optionally other substituents such as chlorine, bromine, lower alkyl such as methyl, lower alkoxy such as methoxy, cyano, nitro, acetylamino or a fibre-reactive group X.

Yet a further class of dyestuffs of the invention are disazo dyes represented by formula (2) wherein A stands for a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series.

The invention also relates to disazo dyestuffs which may be regarded as 2 molecules of the dyestuffs of formula (2) joined together through the radical A by a direct link or a bridging atom or group such as —O—, —S—, —NH—, —CH=CH—, —OCH₂CH₂O—, —CONH— or —NHCONH—.

When the radical A contains a metallisable group, for example a hydroxy or carboxylic acid group, in ortho position to the azo group, then such dyestuffs can form metal complexes, and such metal complexes form further classes of dyestuffs of the invention.

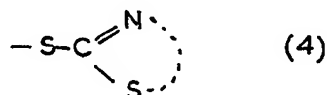
The fibre-reactive group represented by X is a group whose presence in the dyestuff molecule renders the dyestuff capable of chemically combining with hydroxy groups present in cellulose textile materials or with amino groups present in polyamide textile materials. The fibre-reactive groups represented by X are attached to carbon atoms present in the dyestuff molecule and preferably to carbon atoms of aromatic rings, especially benzene rings, present in the dyestuff molecule.

As examples of fibre-reactive groups there may be mentioned acylamino radicals derived from olefinically unsaturated aliphatic carboxylic acids such as acryloylamino and crotonylamino, or from halogen-substituted aliphatic carboxylic acids such as β -chloropropionylamino, β -bromopropionylamino and β : γ : γ -trichlorocrotonylamino. Alternatively X can be a vinyl sulphone, β -chloroethyl sulphone, β -sulphatoethylsulphonyl, β -chloroethylsulphonamide or an optionally N substituted β -aminoethylsulphonyl group.

The fibre-reactive group is preferably a heterocyclic radical having two or three nitrogen atoms in the heterocyclic ring and at least one labile substituent attached to a carbon atom of the heterocyclic ring, a labile substituent being one replaced by the substrate molecule during the colouration process. As examples of labile substituents there may be mentioned chlorine, bromine, quaternary ammonium groups, thiocyanate, sulphonic acid, hydrocarbylsulphonyl groups, groups of the formula $-\text{SC}-\text{N}<$ (3)



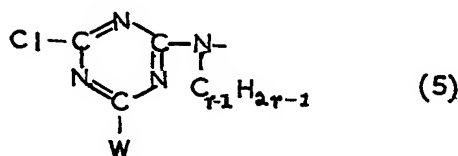
wherein the nitrogen atom carries optionally substituted hydrocarbon or heterocyclic radicals, and groups of the formula:



wherein the dotted line indicates the atoms necessary to form an optionally substituted or fused heterocyclic ring.

As specific examples of such fibre-reactive heterocyclic radicals there may be mentioned 2:3-dichloroquinoxaline -5- or -6-(sulphonyl or carbonyl)amino, 2:4-dichloroquinazoline -6- or 7-sulphonylamino, 2:4:6-trichloroquinazoline-7- or 8-sulphonylamino, 2:4:7- or 2:4:8-trichloroquinazoline-6-sulphonylamino, 2:4-dichloroquinazoline - 6 - carbonylamino, 1:4 - dichlorophthalazine - 6 - carbonylamino, 4:5 - dichloropyridazon - 1 - yl-amino, 2:4 - dichloropyrimid - 5 - yl-carbonylamino, 1 - (phenyl - 4' - carbonylamino) - 4:5 - dichloropyridazone, 1-(phenyl - 4' - sulphonylamino) - 4:5 - dichloropyridazone, 2:4- and/or 2:6-dichloro- or bromo- pyrid-6- (and/or -4)yl-amino, trichloropyrimidylamino, tribromopyrimidylamino, dichloro-5-(cyano, nitro, methyl or methoxycarbonyl)pyrimidylamino, 2 - methylsulphonyl - 6 - chloropyrimid - 4 - ylcarbonylamino and 5 - chloro - 6-methyl-2-methylsulphonylpyrimid-4-yl-amino, and more particularly 1:3:5-triazin-2-yl-amino radicals which contain a bromine and, above all, a chlorine atom on at least one of the 4- and 6-positions, for example 4:6-dichloro-1:3:5-triazin-2-yl-amino. When the triazine nucleus contains only a single chlorine atom then the third carbon atom of the triazine ring can be substituted by a hydrocarbon radical, such as methyl or phenyl, but more particularly by an optionally substituted hydroxy, mercapto or amino group, such as methoxy, phenoxy, α - and β -naphthoxy, methylmercapto, phenylthio, methylamino, diethylamino, cyclohexylamino and anilino and N-alkylanilino and substituted derivatives thereof such as anisidino, toluidino, carboxylanilino, sulphanilino, disulphanilino and sulphonated naphthylamino.

Thus, a preferred class of the azo dyestuffs of the invention comprises those dyestuffs which contain as the fibre-reactive group a group of the formula:



wherein r is 1 or 2, and W is a chlorine atom, an optionally substituted amino group or an etherified hydroxyl group.

The optionally substituted amino groups represented by W are preferably optionally substituted alkylamino, anilino, or N-alkylanilino groups, e.g. methylamino, ethylamino, β -hydroxyethylamino, di-(β -hydroxyethyl)amino, β -methoxyethylamino, β -sulphatoethylamino, anilino, *o*-, *m*- and *p*-sulphanilino, 4- and 5-sulpho-2-carboxyanilino, 4- and 5-sulpho-2-methoxyanilino, 4- and 5-sulpho-2-methylanilino, 4- and

5-sulpho-2-chloroanilino, 2,4-, 2,5- and 3,5-disulphoanilino or N-methyl-*m*- and *p*-sulphoanilino.

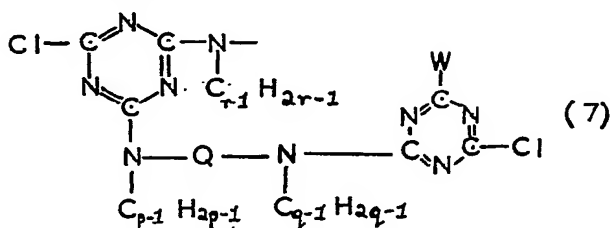
If desired the fibre-reactive group can be of the type:



5 wherein L^1 is a pyrimidine or triazine ring optionally carrying a labile substituent as defined above, L^2 is a pyrimidine or triazine ring carrying at least one labile substituent and Q is a bridging member which is linked to L^1 and L^2 through optionally substituted amino groups, said amino groups being linked together through an alkylene or arylene radical such as ethylene, 1:4-phenylene or 2-sulpho-1:4-phenylene.

10 Other linking groups of particular interest represented by Q are the divalent radicals of stilbene, diphenyl, diphenyloxide, diphenylamine, diphenylurea, diphenoxymethane and diphenylamino-*s*-triazine, which contain a sulphonic acid group in each benzene nucleus.

15 It is preferred that L^1 and L^2 should each represent a chloro-*s*-triazine group. Thus, a further class of the azo dyestuffs of the invention comprises those dyestuffs which contain as the fibre-reactive group a group of the formula:

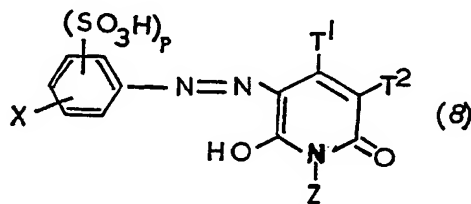


wherein r, p and q are each independently 1 or 2, and W and Q have the meanings stated above.

20 The group W, as previously defined, includes within its scope groups which contain a chromophoric system linked to the carbon atom of the triazine ring through $-\text{NH}-$ or $-\text{O}-$. Such chromophoric systems are preferably of the azo, anthraquinone or phthalocyanine series.

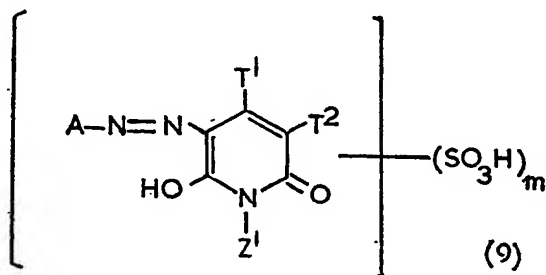
25 Thus, the invention also includes within its scope dyestuffs which may be regarded as comprising two moles of dyes of formula (2) each containing a monohalogeno-*s*-triazinylamino group as the fibre reactive group and which are linked together through the third carbon atoms of each triazine ring by a divalent bridging group.

One class of monoazo dyestuffs of the invention comprises the dyestuffs which, in one of the possible tautomeric forms, are represented by the formula:



30 wherein T^1 , T^2 and Z have the meanings stated, the fibre-reactive group represented by X is attached to the benzene ring in meta or para position to the azo group, and p is 1 or 2.

35 A second class of monoazo dyestuffs of the invention may be represented by the formula:



wherein A represents a benzene or naphthalene nucleus, Z¹ represents an aliphatic radical containing a nitrogen atom to which is attached a cellulose-reactive group,

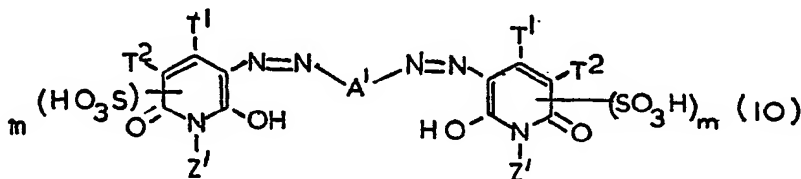
T¹ and T² have the meanings stated above and m is a positive integer.

Preferably Z¹ represents an alkylene radical of 2 to 6 carbon atoms carrying an amino group on the ω-carbon atom which amino group in turn carries the cellulose-reactive group.

The radical represented by A in formula (9) is a naphthalene nucleus or a benzene nucleus preferably carrying at least one sulphonic acid or carboxylic acid and optionally other substituents such as chlorine, bromine, lower alkyl such as methyl, lower alkoxy such as methoxy, cyano, nitro, acetyl amino or a cellulose-reactive group.

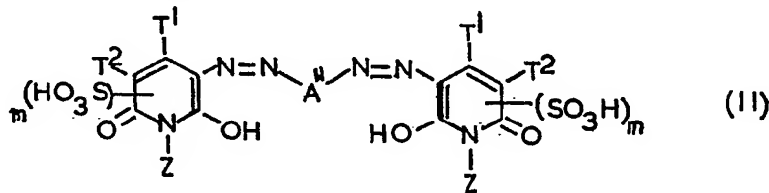
Yet a further class of monoazo dyes of the invention may be represented by formula (9) wherein A, T¹, T² and m have the meanings stated but Z¹ represents a benzene radical containing a cellulose reactive group attached through an amino group to the benzene nucleus and which may be further substituted, e.g. by CH₃, CH₃O or Cl.

Still further classes of dyes of the invention are disazo dyes represented by formula (9) in which T¹, T², Z¹ and m have the meanings already stated and A represents a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series, or dyes of the general formula:

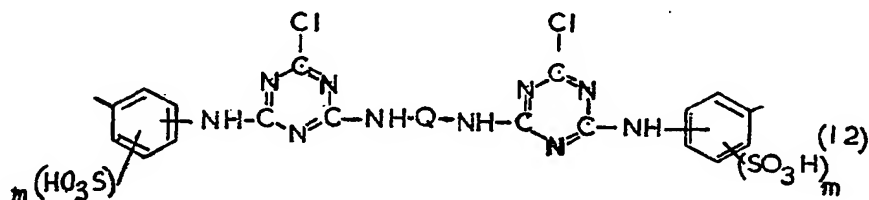


in which T¹, T², Z¹ and m have the meanings stated above, and A¹ stands for a divalent aromatic radical, e.g. phenylene, naphthylene, diphenylene, diphenyloxide, stilbene, diphenylamine, diphenylurea, diphenoxyethane which preferably contain at least one SO₃H group.

A further class of disazo dyes of the invention are represented by the formula:

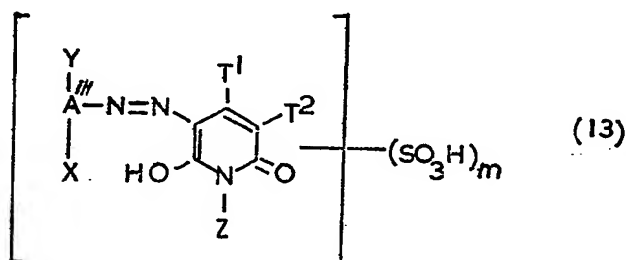


in which T¹, T², Z and m have the meanings stated earlier and A'' represents a divalent aromatic radical which contains at least one fibre reactive group, e.g. a 2-chloro-4,6-diphenyl-s-triazine group or a group of the formula:



where Q has the meaning stated above and m stands for 1 or 2. In the field of metal-complex dyes of the invention there are a number of classes which correspond in general terms with formula (8) to (11) above. Included amongst these are the following classes:

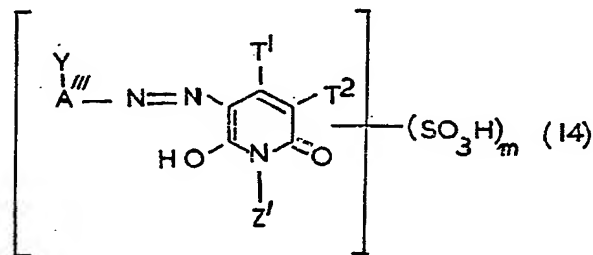
(1) 1:1-copper and nickel complexes of monoazo compounds of the formula:



wherein Y stands for a hydroxyl or carboxylic acid group,

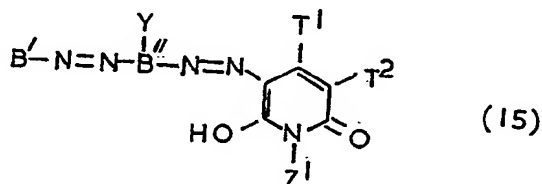
A''' stands for a benzene or naphthalene nucleus having Y *ortho* to the azo group, and X, T¹, T², Z and m have the meanings already stated;

(2) 1:1 copper and nickel complexes and 1:2 chromium and cobalt complexes of monoazo compounds of the formula:



wherein Y, A''', T¹, T², Z¹ and m have the meanings stated above.

(3) 1:1 copper and nickel complex of disazo compounds of the formula:

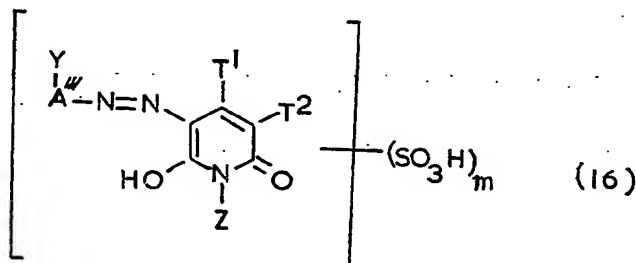


in which B' represents a benzene or naphthalene nucleus containing at least one and preferably more than one SO₃H group, B'' represents a 1,4-phenylene nucleus which may also be substituted by CH₃ or CH₂O, and Y, T¹, T² and Z¹ have the meanings stated above.

A preferred class of these disazo compounds may be represented by formula (9) above, wherein m is a positive integer, T¹ and T² have the meanings stated above, Z¹ represents an aliphatic radical containing a nitrogen atom to which is attached a cellulose reactive group, more especially an alkylene radical of 2-6 carbon atoms carrying an amino group on the ω -carbon atom which amino group in turn carries the cellulose

reactive group, and A represents an azobenzene radical in which the benzene nucleus adjacent to the pyridone nucleus carries a *o*-hydroxyl group and optionally a methyl or methoxy group whilst the other benzene nucleus is substituted by one or two sulphonic acid groups.

(4) cobalt or chromium complexes containing 1 mole of a monoazo compound of the formula:

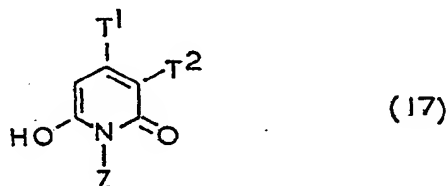


wherein A'', Y, T¹, T², Z and m have the meanings stated above and 1 mole of a polydentate ligand containing a cellulose-reactive group linked to the Co or Cr atom.

In the above classes, the reactive group can take any of the forms represented by formulae 5, 6 and 7.

The new dyestuffs can be obtained by the conventional coupling and where necessary condensation and/or metallisation reactions used for manufacture of cellulose-reactive dyestuffs characterised by use in the coupling stage of a 2,6-dihydroxy-pyridine or a 2-hydroxy-pyrid-6-one compound.

Thus the metal-free azo dyestuffs of the invention may be obtained by diazotising an aromatic amine and coupling the resulting diazo compound with a coupling component which in one of the possible tautomeric forms is represented by the formula:



wherein T¹, T² and Z have the meanings stated above, the amine and the coupling component together containing at least one fibre-reactive group, and at least one sulphonic acid group.

The diazotisation and coupling stages of this process can be carried out in conventional manner, but are preferably carried out in an acid or at most weakly alkaline aqueous medium so as to reduce the possibility of hydrolysis of the fibre-reactive groups present.

Amines of the formula A—NH₂ which contain a fibre-reactive group can be obtained by condensing a compound of the formula X-halogen with the appropriate diamine, for example with 1:4-phenylenediamine-2:5-disulphonic acid, under such conditions that only one of the two amino groups reacts with the compound of the formula X halogen.

Coupling components of formula 17 which contain a fibre-reactive group can be obtained by condensing the appropriate coupling component containing an amino group with one molecular proportion of a compound of the formula X halogen.

The coupling components of formula 17 which do not contain a fibre-reactive group and those containing a group, such as an amino group, which can subsequently be converted to a fibre-reactive group can themselves be obtained by a number of methods such as are described for example, in "Heterocyclic Compounds — Pyridine and its derivatives — Part 3" which was edited by Klingsberg and published by Interscience Publishers in 1962. Typical methods include, for example, (1) condensing together compounds of the formula T¹COCH₂COO alkyl and T²CH₂COO alkyl in the presence of an excess of an amine of the formula Z—NH₂, (2) cyclisation of an

$\alpha:\beta$ -disubstituted glutaconamide of the formula $\text{alkyl OOC}\cdot\text{CH}_2\text{C}=\overset{\text{T}^2}{\underset{\text{T}^1}{\text{C}}}\text{CONHZ}$, which

is itself obtained by condensing together in the presence of a basic catalyst compounds of the formulae $\text{T}^1\text{COCH}_2\text{COO alkyl}$ and $\text{T}^2\text{CH}_2\text{CONHZ}$, or (3) cyclisation of an

$\alpha:\beta$ -disubstituted glutaconamide of the formula: $-\text{ZNHCOCH}_2\text{C}=\overset{\text{T}^2}{\underset{\text{T}^1}{\text{C}}}\cdot\text{COO alkyl}$

5 which is itself obtained by condensing together compounds of the formulae $\text{T}^1\text{COCH}_2\text{CONHZ}$ and $\text{T}^2\text{CH}_2\text{COO alkyl}$. 5

As specific examples of coupling compounds of formula 17 which do not contain a fibre-reactive group there may be mentioned 2:6-dihydroxypyridine, 2:6-dihydroxy-3-cyano-4-methyl-pyridine, 1-(methyl or ethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one, 1-(β -hydroxyethyl or γ -methoxypropyl)-3-cyano-4-(methyl, phenyl or ethyl)-6-hydroxypyrid-2-one, 1-(phenyl, *p*-tolyl or *p*-anisyl)-3-cyano-4-(methyl or phenyl)-6-hydroxypyrid-2-one, 1-phenyl-3-(aminocarbonyl, carboxy or ethoxycarbonyl)-4-(methyl or phenyl)-6-hydroxypyrid-2-one, 2:6-dihydroxy-3-(aminocarbonyl, ethoxycarbonyl, diethylaminocarbonyl)-4-methylpyridine, 2:6-dihydroxy-3-(aminocarbonyl or ethoxycarbonyl)pyridine, 2:6-dihydroxy-3-aminocarbonyl-4-phenyl pyridine, 2:6-dihydroxy-3-cyano-4-aminocarbonyl pyridine, 2:6-dihydroxy-3-cyano-4-(carboxy, methoxycarbonyl or ethoxycarbonyl)pyridine, ethyl 2:6-dihydroxy-3-cyanopyrid-4-yl-acetate, 2:6-dihydroxy-3-cyanopyrid-4-ylacetamide, 2:6-dihydroxy-3:4-di(carboxy or ethoxycarbonyl)pyridine, 2:6-dihydroxy-3-aminocarbonyl-4-ethoxycarbonyl-pyridine, 2:6-dihydroxy-4-methylpyridine, ethyl 2:6-dihydroxy iso-nicotinate, 2:6-dihydroxy isonicotinamide, 2:6-dihydroxy iso-nicotinic acid diethylamide, 2:6-dihydroxy-4-cyanopyridine, 2:6-dihydroxy-4-phenylpyridine, 2:6-dihydroxy-4-(*p*-hydroxyphenyl)pyridine, 2:6-dihydroxy-4-(*p*-methoxyphenyl)pyridine, 2:4:6-trihydroxypyridine, 2:6-dihydroxy-3-cyano-4-ethoxycarbonylmethylpyridine, 4-methyl-1-ethyl-3-aminocarbonyl-6-hydroxy-pyrid-2-one and 4-methyl-1-phenyl-3-aminocarbonyl-6-hydroxypyrid-2-one. 10 15 20 25

As examples of coupling components containing an amino group, there may be mentioned compounds of formula 17 in which Z represents an aliphatic radical containing an amino group or a phenyl radical containing an amino group.

Those in which Z represents an aliphatic radical containing an amino group can be obtained by the methods just described, but using as the amine of formula $\text{Z}-\text{NH}_2$ a substantial excess of an aliphatic diamine. As examples of such coupling components there may be mentioned:

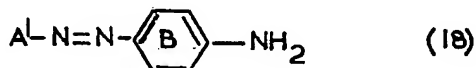
N - β - aminoethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, N - β -aminoethyl - 3 - cyano - 4 - phenyl - 6 - hydroxypyrid - 2 - one, N - γ - amino-propyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, N - (β - aminoethyl)-3 - carboxy - 4 - methyl - 6 - hydroxypyrid - 2 - one, N - β - aminoethoxyethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, N - β - aminopropyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, N - β - aminopropyl - 3 - cyano - 4 - phenyl-6 - hydroxypyrid - 2 - one, N - (N - aminoethylamino)ethyl - 3 - cyano - 4 - methyl-6 - hydroxypyrid - 2 - one, N - (β - aminoethyl) - 3 - cyano - 4 - carboxyethyl - 6-hydroxypyrid - 2 - one, N - (β - aminoethyl) - 3 - cyano - 4 - cyclohexyl - 6-hydroxypyrid - 2 - one, N - (β - aminoethyl) - 3 - cyano - 4 - (3' - pyridyl) - 6-hydroxypyrid - 2 - one, N - (β - aminopropyl) - 3 - cyano - 4 - carbondimethylamido-6 - hydroxypyrid - 2 - one, N - β - methylaminoethyl - 3 - cyano - 4 - methyl - 6-hydroxypyrid - 2 - one, N - β - phenylaminoethyl - 3 - cyano - 4 - methyl - 6-hydroxypyrid - 2 - one, and N - β - ethylaminoethyl - 3 - cyano - 4 - methyl - 6-hydroxypyrid-2-one. 35 40 45

Those in which Z represents a phenyl radical containing an amino group can be obtained by the methods just described, but using as the amine of formula $\text{Z}-\text{NH}_2$ an excess of a nitroaniline, which may be substituted, e.g. by methyl, methoxy or chlorine, followed by a reduction treatment to convert the nitro group to amino. As examples of such coupling components there may be mentioned:

1-(3'-aminophenyl)-3-cyano and -3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-ones, 1-(4'-aminophenyl)-3-cyano and -3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-ones, 50 55

1-(3'-amino-4-methylphenyl)-3-cyano and -3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-ones, and 1-(3'-amino-4'-methoxyphenyl)-3-cyano and -3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-ones.

- As examples of compounds of the formula X-halogen which can be reacted with amines of the formula A—NH₂ or coupling components of formula 17 which contain an additional amino group to give dyestuff intermediates containing a fibre-reactive group there may be mentioned acryloyl chloride, β-chloropropionyl chloride, β-bromopropionyl bromide, chloroacetyl chloride, α:β-dichloropropionyl chloride, 2:3-dichloroquinoxaline-5- or 6-carbonyl chloride, 2:3-dichloroquinazoline-5- or -6-sulphonyl chloride, 2:4-dichloroquinazoline-6- or 7-sulphonyl chloride, 2:4:6-trichloroquinazoline-7- or 8-sulphonyl chloride, 2:4:7- or 2:4:8-trichloroquinazoline-6-sulphonyl chloride, 2:4-dichloroquinazoline-6-carbonylchloride, 2:4-dichloropyrimidine - 5 - carbonyl chloride, 2 - methylsulphonyl - 6 - chloropyrimidine - 4-carbonyl chloride, β-(4:5-dichloropyridazon-1-yl)propionyl chloride, 1-(phenyl)-4'-carbonyl chloride)-4:5-dichloro-6-pyridazone, 1-(phenyl-4'-chlorosulphonyl)-4:5-dichloro-6-pyridazone, 2:4:6-trichloropyrimidine, 2:4:6-tri(chloro or bromo)-5-(methyl, nitro- or cyano)pyrimidine, tetrafluorocyclobutane carbonyl chloride, trifluorocyclobutene carbonyl chloride, β-(tetrafluorocyclobutyl)acryloyl chloride, β-(trifluorocyclobutenyl)acryloyl chloride, 2:4:5:6-tetrachloropyrimidine, 2:4-dichloro-5-nitro-6-methylpyrimidine, 5-ethoxycarbonyl-2:4:6-trichloropyrimidine, 2:4:6-tribromopyrimidine, 2:4:6-trifluoropyrimidine, cyanuric chloride, cyanuric bromide, the primary condensation products of cyanuric chloride with ammonia, amines, organic hydroxy or mercapto compounds, such as methanol, ethanol, phenol, α-naphthol, β-naphthol, chlorophenols, cresols, sulphonated phenols, thiophenol, thioglycolic acid, methyl mercaptan, dimethyldithiocarbamic acid, 2-mercaptobenzthiazole, thioacetamide, primary alkylamines such as methylamine, ethylamine, *n*-propylamine, dimethylamine and diethylamine, β-hydroxy ethylamine, di(β-hydroxyethyl)amine, piperidine, morpholine, β-methoxyethylamine, aminoacetic acid, aniline, *N*-methyl-aniline, toluidine, anisidine, aniline-2:5-, 2:4- and 3:5-disulphonic acids, aniline *o*-, *m*- and *p*-sulphonic acid, *N*-methylaniline *o*-, *m*- and *p*-sulphonic acid, *o*-, *m*- and *p*-aminobenzoic acid, 4- and 5-sulpho-2-aminobenzoic acid, 2-aminotoluene-4-sulphonic acid, 5-amino-2-hydroxybenzoic acid, β-aminoethane sulphonic acid, *N*-methylaminoethane sulphonic acid and mono- and di-sulphonic acids of 1-amino- and 2-amino-naphthalene.
- As specific examples of amines of the formula A—NH₂ free from fibre-reactive groups which can be coupled with coupling components of formula 17 which contain a fibre-reactive group there may be mentioned aniline-2-, 3- and 4-sulphonic acids, aniline-2:5-, 2:4- and 3:5-disulphonic acid, 2-aminophenol-4- or 6-sulphonic acid, 4- or 5-sulpho-2-aminobenzoic acid, 4-(or 6-)chloro-2-aminophenol-6-(or 4-)sulphonic acid, 4-(or 6-)nitro-2-aminophenol-6-(or 4-)sulphonic acid, 2-aminophenol-4:6-disulphonic acid, 4(nitro, acetyl-amino- or methoxy), aniline-2-sulphonic acid, 1-naphthylamine-3-, 4-, 5-, 6-, 7- or 8-sulphonic acid, 2-aminonaphthalene-1-, 5-, 6-, 7- or 8-sulphonic acid, 1-naphthylamine-3:6:8- and 2:5:7-trisulphonic acid, 1-naphthylamine, 2:7-, 3:6-, 3:8-, 4:6- and 4:7-disulphonic acid, 2-naphthylamine, 1:5-, 3:7-, 4:8-, 5:7- and 6:8-disulphonic acid, 2-naphthylamine-3:6:8-trisulphonic acid, 4-amino-4'-nitro-2:2'-disulphostilbene, anthranilic acid and 4-aminophenol-2-carboxylic acid. Included within the scope of amines of the formula A—NH₂ are amines of the formula:—



- wherein A¹ is an optionally substituted phenyl or naphthyl radical and the benzene ring B can contain substituents or form part of an optionally substituted naphthalene ring. As specific examples of such amines there may be mentioned 4-(2':5'-disulphophenylazo)aniline, 4-(2':5'-disulphophenylazo)-2:5-dimethoxyaniline and 4-(*p*-sulphophenylazo)-1-naphthylamine-6- or 7-sulphonic acid.

- As specific examples of diamines free from fibre-reactive groups but which contain two radicals A joined together through a direct link or a bridging atom or group and which are tetrazotised and coupled with two molecular proportions of a coupling component of Formula 17 containing a fibre-reactive group to give disazo dyestuffs of the invention there may be mentioned benzidine-2:2'-disulphonic acid,

4:4'-diaminodiphenylurea-2:2'-disulphonic acid, 4:4'-diaminostilbene-2:2'-disulphonic acid and 4:4'-diaminodiphenoxyethane-2:2'-disulphonic acid.

As specific examples of compounds which can be reacted with one molecular proportion of a compound of formula $X-Cl$ to give amines of formula $A-NH_2$ containing a fibre-reactive group there may be mentioned 1:3-phenylenediamine-4-sulphonic acid, 1:4-phenylenediamine-2-sulphonic acid, 1:3-phenylenediamine-4:6-disulphonic acid, 1:4-phenylenediamine-3:6-disulphonic acid and 2:6-diaminonaphthalene-4:8-disulphonic acid.

The following Examples and table depict typical dyestuffs of the invention and their manufacture by coupling; parts are by weight:

EXAMPLE 1

A solution of 7.4 parts of cyanuric chloride in 50 parts of acetone is added with stirring to 100 parts of water at 0° to $4^\circ C$. A solution of the sodium salt of 7.52 parts of 1:3-diaminobenzene-4-sulphonic acid in 120 parts of water is then added, the temperature of the mixture being maintained at 0° to $4^\circ C$. by external cooling. After the reaction is complete the pH of the mixture is raised to between 6.5 and 7 by the addition of sodium carbonate and a solution of the sodium salt of 6.93 parts of metanilic acid in 100 parts of water is added. The mixture is then stirred for 4 hours at 30° to $40^\circ C$. while the pH of the mixture is maintained between 4.5 and 6 by the addition of sodium carbonate. The resulting solution is cooled to $0^\circ C$., 20 parts of a 2N aqueous solution of sodium nitrite are added, followed by 12 parts of a concentrated aqueous solution of hydrochloric acid. The mixture is stirred for 30 minutes and the excess nitrous acid is then destroyed by addition of sulphamic acid. The resulting mixture containing the diazo compound is added with stirring to a slightly alkaline solution of 6 parts of 2:6-dihydroxy-3-cyano-4-methylpyridine in 200 parts of water at 0° to $4^\circ C$., and the pH is adjusted to between 7.5 and 8.0. After coupling is completed, acetic acid is added to lower the pH to 6.0, the temperature is raised to $20^\circ C$., and the dyestuff precipitated by the addition of sodium chloride. The dyestuff is then filtered off and dried.

When applied to cotton and viscose rayon textile materials in conjunction with a treatment with an acid-binding agent the dyestuff yields bright greenish-yellow shades having excellent fastness to wet treatments such as washing and to light.

EXAMPLE 2 to EXAMPLE 153

The following Table depicts further examples of the invention obtained in similar manner to Example 1 by condensing the diamine named in column II with one mole of the acid chloride compound named in column I and diazotising and coupling the resultant amino compound with the coupling component named in column III. The shade of the dyestuff obtained is stated in the final column.

Example	I	II	III	IV Shades
2	cyanuric chloride	1,3-diaminobenzene-4,6-disulphonic acid	2,6-dihydroxy-3-cyano-4-methylpyridine	Greenish-Yellow
3	— do —	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
4	— do —	— do —	1-β-hydroxyethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
5	— do —	— do —	1-isopropyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
6	— do —	1,4-diaminobenzene-3,6-disulphonic acid	2,6-dihydroxy-3-cyano-4-methylpyridine	Reddish-Yellow
7	— do —	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
8	— do —	— do —	1-β-hydroxyethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
9	2,4-dichloro-6- <i>m</i> -sulphoamino- <i>s</i> -triazine	1,4-diaminobenzene-3,6-disulphonic acid	— do —	— do —
10	— do —	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
11	— do —	1,3-diaminobenzene-4,6-disulphonic acid	— do —	Greenish-Yellow
12	— do —	— do —	1-β-hydroxyethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
13	— do —	— do —	1-isopropyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —

Example	I	II	III	IV Shade
14	2,4-dichloro-6- <i>m</i> -sulphoanilino- <i>s</i> -triazine	2,6-diaminonaphthalene-4,8-disulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	Orange
15	2,4-dichloro-6-N- α -sulphomethylanilino- <i>s</i> -triazine	1,3-diaminobenzene-4,6-disulphonic acid	2,6-dihydroxy-3-cyano-4-methylpyridine	Greenish Yellow
16	— do —	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
17	2,4-dichloro-6-N-methyl- <i>m</i> -sulphoaniline- <i>s</i> -triazine	— do —	— do —	— do —
18	2,4-dichloro-6-(2'-methyl-5'-sulpho)-anilino- <i>s</i> -triazine	— do —	— do —	— do —
19	2,4-dichloro-6-(2',5'-disulpho)-anilino- <i>s</i> -triazine	— do —	— do —	— do —
20	2,4-dichloro-6-(3',6',8'-trisulpho)-naphth-2'-ylamine- <i>s</i> -triazine	— do —	— do —	— do —
21	4,5-dichloro-6-methyl-2-methylsulphonylpyrimidine	— do —	— do —	— do —

Example	I	II	III	IV Shade
22	2,3-dichloroquinoxaline-6-carbonyl chloride	1,3-diaminobenzene-4,6-disulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	Greenish-Yellow
23	β -(4,5-dichloropyridaz-3-onyl-1-propionyl chloride	— do —	— do —	— do —
24	β -acetoxypionyl chloride	— do —	— do —	— do —
25	acryloyl chloride	— do —	— do —	— do —
26	β -phenylsulphonyl propionyl chloride	— do —	— do —	— do —
27	3,6-dichloropyridazine-4-carbonyl chloride	— do —	— do —	— do —
28	2,4,6-trichloropyrimidine	— do —	— do —	— do —
29	2,4,5,6-tetrachloropyrimidine	— do —	— do —	— do —
30	5-bromo-2,4,5-trichloropyrimidine	— do —	— do —	— do —
31	5-cyano-2,4,5-trichloropyrimidine	— do —	— do —	— do —
32	2,4-dichloropyrimidine-5-carbonyl chloride	— do —	— do —	— do —

Example	I	II	III	IV Shade
33	2,4-dichloropyrimidine-5-sulphonyl chloride	1,3-diaminobenzene-4,6-disulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	Greenish-Yellow
34	2-chlorobenzthiazole-6-carbonyl chloride	— do —	— do —	— do —
35	1,4-dichlorophthalazine-6-carbonyl chloride	— do —	— do —	— do —
36	β -bromopropionyl bromide	— do —	— do —	— do —
37	cyanuric chloride	— do —	1,4-dimethyl-3-cyano-6-hydroxypyrid-2-one	— do —
38	2,4-dichloro-6-sulphoanilino- <i>s</i> -triazine	— do —	— do —	— do —
39	2,4-dichloro-6-(3',5'-disulpho)-anilino <i>s</i> -triazine	1,4-phenylenediamine-2-sulphonic acid	— do —	Reddish-Yellow
30	2,4-dichloro-6- <i>m</i> -sulphoanilino- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	1-cyclohexyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	Greenish-Yellow
41	— do —	— do —	1- β -methoxypropyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
42	— do —	— do —	1- β -dimethylaminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
43	— do —	— do —	2,6-dihydroxynicotinic acid	— do —

Example	I	II	III	IV Shade
44	2,4-dichloro-6- <i>m</i> -sulphoanilino- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	2,6-dihydroxy-pyridine	Greenish Yellow
45	— do —	— do —	2,6-dihydroxy-4-methylpyridine	— do —
46	— do —	— do —	2,6-dihydroxy-4-phenylpyridine	— do —
47	— do —	— do —	2,6-dihydroxy-4-(4'-methoxy-phenyl)pyridine	— do —
48	— do —	— do —	2,6-dihydroxy-4-(3'-methyl-phenyl)pyridine	— do —
49	— do —	— do —	2,6-dihydroxy-3-methylpyridine	— do —
50	— do —	— do —	2,6-dihydroxy-3-phenylpyridine	— do —
51	— do —	— do —	2,6-dihydroxy-3-benzylpyridine	— do —
52	— do —	— do —	2,6-dihydroxy-3,4-dimethylpyridine	— do —
53	— do —	— do —	2,6-dihydroxy-3-ethyl-4-methylpyridine	— do —
54	— do —	— do —	2,6-dihydroxy-3-benzyl-4-methylpyridine	— do —
55	— do —	— do —	2,6-dihydroxy-4-aminopyridine	— do —
56	— do —	— do —	2,6-dihydroxy-4-aminocarbonylpyridine	— do —
57	— do —	— do —	Ethyl-2,6-dihydroxypyrid-4-yl acetate	— do —

Example	I	II	III	IV Shade
58	2,4-dichloro-6- <i>n</i> -sulphoanilino- <i>s</i> - triazine	1,3-phenylenediamine-4,6- disulphonic acid	2,4,6-trihydroxypyridine	Greenish- Yellow
59	— do —	— do —	2,6-dihydroxy-4-ethoxy-carbonyl- pyridine	— do —
60	— do —	— do —	2,6-dihydroxy-3-ethoxy-carbonyl- pyridine	— do —
61	— do —	— do —	2,6-dihydroxynicotinic acid	— do —
62	— do —	— do —	2,6-dihydroxy-3-aminocarbonyl- pyridine	— do —
63	— do —	— do —	2,6-dihydroxy-3-nitropyridine	— do —
64	— do —	— do —	2,6-dihydroxy-3-methylpyridine-4- carboxylic acid	— do —
65	— do —	— do —	2,6-dihydroxy-3-methyl-4-hydroxy- pyridine	— do —
66	— do —	— do —	2,6-dihydroxy-3-methyl-4-amino- pyridine	— do —
67	— do —	— do —	2,6-dihydroxy-3-(3'-chlorophenyl)- 4-aminocarbonylpyridine	— do —
68	— do —	— do —	2,6-dihydroxy-3-ethoxycarbonyl-4- methylpyridine	— do —
69	— do —	— do —	2,6-dihydroxy-3-aminocarbonyl-4- methylpyridine	— do —
70	— do —	— do —	2,6-dihydroxy-4-phenylnicotinic acid	— do —

Example	I	II	III	IV Shade
71	2,4-dichloro-6- <i>m</i> -sulphoanilino- <i>s</i> - triazine	1,3-phenylenediamine-4,6- disulphonic acid	2,6-dihydroxy-3,4-ethoxy-carbonyl- pyridine	Greenish- Yellow
72	— do —	— do —	2,6-dihydroxy-3-amino-4-ethoxy- carbonylpyridine	— do —
73	— do —	— do —	2,6-dihydroxy-3-cyano-4-phenyl- pyridine	— do —
74	— do —	— do —	Ethyl-2,6-dihydroxy-3-cyano- pyrid-4-ylacetate	— do —
75	— do —	— do —	2,6-dihydroxy-3-cyano-pyrid-4-yl- acetamide	— do —
76	— do —	— do —	1,4-diphenyl-6-hydroxy-pyrid-2-one	— do —
77	— do —	— do —	1-(4'-methoxyphenyl)-4-methyl-6- hydroxypyrid-2-one	— do —
78	— do —	— do —	1-phenyl-4-(4'-methoxyphenyl)-6- hydroxypyrid-2-one	— do —
79	— do —	— do —	1-methyl-3-cyano-4-phenyl-6- hydroxypyrid-2-one	— do —
80	— do —	— do —	1-ethyl-3-cyano-4-amino-6-hydroxy- pyrid-2-one	— do —

Example	I	II	III	IV Shade
81	2,4-dichloro-6-(2',5'-disulpho- anilino)-s-triazine	1,3-phenylenediamine-4-sulphonic acid	2,6-dihydroxyisonicotinic acid	Greenish- Yellow
82	cyanuric chloride	1,4-phenylene diamine-2,5- disulphonic acid	— do —	Yellow
83	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- s-triazine	— do —	— do —	— do —
84	cyanuric chloride	1,3-phenylene diamine-4,6- disulphonic acid	2,6-dihydroxynicotinic acid	Greenish- Yellow
85	2,4,5,6-tetrachloropyrimidine	— do —	— do —	— do —
86	2,4-dichloro-6-(<i>p</i> -sulphoanilino)- s-triazine	1,4-phenylene diamine-2,5- disulphonic acid	2,6-dihydroxy-3-ethoxycarbonyl- pyridine	Yellow
87	2,4-dichloro-6-(2'-methyl-5'- sulphoanilino)-s-triazine	— do —	2,6-dihydroxy-4-aminocarbonyl pyridine	— do —
88	2,4-dichloro-6-(<i>N</i> - ω -sulpho- methylanilino)-s-triazine	1,3-phenylene diamine-4,6- disulphonic acid	— do —	Greenish- Yellow
89	2-methylsulphonyl-6-methyl- 4,5-dichloropyridine	— do —	2,6-dihydroxy-3,4-dimethyl- pyridine	— do —

Example	I	II	III	IV Shade
90	acryloyl chloride	1,3-phenylenediamine-4,6-disulphonic acid	2,6-dihydroxy-3,4-dimethylpyridine	Greenish-Yellow
91	1-(4'-chloro-carbonylphenyl)-dichloro-pyridaz-6-one	— do —	2,6-dihydroxy-4-methylpyridine	— do —
92	2,4,6-trichloro-5-cyanopyrimidine	— do —	— do —	— do —
93	2,3-dibromopropionyl chloride	— do —	2,6-dihydroxy-iso-nicotinic acid	— do —
94	tetrafluorocyclo-butane-carbonyl chloride	— do —	2,6-dihydroxy-4-methylpyridine	— do —
95	trifluoro-cyclo-butene-carbonyl chloride	— do —	2,6-dihydroxy-4-methylpyridine	— do —
96	β -(tetrafluorocyclobutyl)acryloyl chloride	— do —	2,6-dihydroxy-3,4-dimethylpyridine	— do —
97	β -(trifluorocyclobutenyl)acryloyl chloride	— do —	— do —	— do —
98	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	— do —	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —

Example	I	II	III	IV Shade
99	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	1-methyl-3-aminocarbonyl-4-methyl-6-hydroxy-pyrid-2-one	Greenish-Yellow
100	— do —	— do —	1- <i>n</i> -propyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
101	— do —	1,4-phenylenediamine-2,5-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Reddish-Yellow
102	cyanuric chloride	— do —	— do —	— do —
103	2,4-dichloroquinazoline-5-carbonyl chloride	— do —	— do —	— do —
104	2,4-dichloropyrimidine-5-carbonyl chloride	1,3-phenylenediamine-4,6-disulphonic acid	— do —	Greenish-Yellow
105	2,4,5,6-tetrachloro-pyrimidine	— do —	— do —	— do —
106	2,3-dichloroquinoxaline-6-carbonyl chloride	— do —	— do —	— do —
107	2,4-dichloro-6-(2'-methyl-5'-sulpho-anilino)- <i>s</i> -triazine	— do —	— do —	— do —
108	— do —	— do —	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	— do —
109	cyanuric chloride	— do —	— do —	— do —

Example	I	II	III	IV Shade
110	2,4-dichloro-6-methoxy-s-triazine	1,3-phenylenediamine-4,6-disulphonic acid	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	Greenish-Yellow
111	— do —	— do —	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
112	2,4-dichloro-6-(2',5'-disulpho-anilino)-s-triazine	1,3-phenylenediamine-4-sulphonic acid	— do —	— do —
113	2,4-dichloro-6-(3'-sulpho-anilino)-s-triazine	— do —	— do —	— do —
114	cyanuric chloride	1,4-phenylenediamine-2,5-disulphonic acid	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	Reddish-Yellow
115	2,4-dichloro-6-amino-s-triazine	1,3-phenylenediamine-4,6-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Greenish-Yellow
116	2,4-dichloro-6-ethyl-amino-s-triazine	— do —	— do —	— do —

Example	I	II	III	IV
117	Cyanuric chloride	1,3-phenylenediamine-4,6-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Greenish yellow
118	— do —	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —
119	— do —	— do —	1-γ-methoxypropyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
120	— do —	— do —	1-isopropyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
121	— do —	— do —	2,6-dihydroxy-3-diethylamino-carbonyl-4-methylpyridine	— do —
122	— do —	— do —	2,6-dihydroxy-3-dimethylamino-carbonyl-4-methylpyridine	— do —
123	— do —	— do —	1-ethyl-3-(N'-phenylamino-carbonyl)-4-methyl-6-hydroxypyrid-2-one	— do —
124	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —
125	— do —	— do —	1,4-dimethyl-3-aminocarbonyl-6-hydroxypyrid-2-one	— do —
126	— do —	— do —	1,4-diphenyl-3-aminocarbonyl-6-hydroxypyrid-2-one	— do —
127	— do —	— do —	1,4-dimethyl-6-hydroxypyrid-2-one	— do —

Example	I	II	III	IV
128	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	1-phenyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Greenish yellow
129	— do —	— do —	1,4-dimethyl-3-(N'-ethyl-N'-phenylaminocarbonyl)-6-hydroxypyrid-2-one	— do —
130	— do —	— do —	1-ethyl-3-(N'-benzylaminocarbonyl)-4-methyl-6-hydroxypyrid-2-one	— do —
131	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)- <i>s</i> -triazine	1,3-phenylenediamine-4-sulphonic acid	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —
132	— do —	— do —	1-γ-methoxypropyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
133	— do —	2,6-naphthalenediamine-4,8-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Reddish yellow
134	2,4-dichloro-6-(2',5'-disulphoanilino)- <i>s</i> -triazine	— do —	— do —	— do —
135	— do —	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —
136	cyanuric chloride	— do —	1-γ-methoxypropyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —

Example	I	II	III	IV
137	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	1,3-phenylenediamine-4-sulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Greenish yellow
138	2,4-dichloro-6-(4'-sulphoanilino)-s-triazine	1,3-phenylenediamine-4,6-disulphonic acid	— do —	— do —
139	2,4-dichloro-6-amino-s-triazine	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
140	2,4-dichloro-6-hydroxyamino-s-triazine	— do —	— do —	— do —
141	2,4-dichloro-6-amino-s-triazine	— do —	1- β -hydroxyethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
142	2,4-dichloro-6-(2'-methyl-5'-sulpho-anilino)-s-triazine	1,4-phenylenediamine-2,5-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	Reddish yellow
143	2,4-dichloro-6-methoxy-s-triazine	— do —	— do —	— do —
144	2,4-dichloro-6- β -hydroxyethyl-amino-s-triazine	1,3-phenylenediamine-4-sulphonic acid	— do —	Greenish yellow
145	2,4-dichloro-6-(<i>n</i> -sulphoanilino)-s-triazine	1,3-phenylenediamine-4,6-disulphonic acid	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	— do —

Example	I	II	III	IV
146	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	Greenish yellow
147	cyanuric chloride	1,4-phenylenediamine-2,5-disulphonic acid	1-ethyl-4-methyl-6-hydroxypyrid-2-one	Reddish yellow
148	2,4-dichloro-6-(<i>m</i> -sulphoanilino)- <i>s</i> -triazine	— do —	— do —	— do —
149	— do —	— do —	4-methyl-2,6-dihydroxypyridine	— do —
150	2,4-dichloro-6-(2'-methyl-4'-sulphoanilino)- <i>s</i> -triazine	1,3-phenylenediamine-4,6-disulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	Greenish yellow
151	2,4-dichloro-6-(4'-sulphoanilino)- <i>s</i> -triazine	— do —	— do —	— do —
152	2,4-dichloro-6- β -hydroxyethyl-amino- <i>s</i> -triazine	— do —	— do —	— do —
153	2,4-dichloro-6-(4'-sulphophenoxy)- <i>s</i> -triazine	— do —	— do —	— do —

The 1-alkyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-ones used in the above examples are believed to be novel. They may be obtained by hydrolysis of the corresponding 3-cyano compound by treatment with cold acid. A typical preparation of 1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one is as follows:

5 60 Parts of powdered 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one are added
to 330 parts of stirred 100% sulphuric acid during 1 hour, the temperature of the
mixture not being permitted to rise above 20°C. during this time. The mixture is then
10 stirred at 50—55°C. for 24 hours and the resulting clear solution poured onto 600
parts of crushed ice. The white precipitate is collected by filtration and washed by
slurrying with 5% brine solution until the washings are no longer acid to Congo Red
15 indicator paper. The product, after drying in vacuo over phosphorus pentoxide melts
with decomposition at 164° and is found to contain 14.1% N ($C_9H_{12}N_2O_3$ req
N=14.3%). Recrystallisation from alcohol gives well formed prisms melting at 164°
with decomposition, analysis now giving C=54.6%, H=6.2%, N=14.2%, M.W.
by mass spectrum 196 ($C_9H_{12}N_2O_3$ req. C=55.1%, H=6.2%, N=14.3%, M.W.
196).

EXAMPLE 154

20 A solution of 6.7 parts of 1,3-phenylenediamine-4,6-disulphonic acid is 50 parts
of water at 0—5°C. and pH 5.0 is added rapidly with stirring to a suspension prepared
by dissolving 4.63 parts of cyanuric chloride in 25 parts of acetone and adding the
resulting solution to 50 parts of water and 50 parts of ice. The mixture is stirred for
2 hours at 0—5°C. maintaining the pH at 4—5 by addition of 2N sodium carbonate
solution.

25 A solution of 5 parts of 4,4'-diaminodiphenyl urea-2,2'-disulphonic acid in 50
parts of water at pH 6.5 is added rapidly to the solution prepared in the preceding
paragraph and the mixture is stirred and heated at 30—35°C. for 1 hour, the pH being
maintained at 6—7 by adding 2N sodium carbonate solution.

30 The solution is then cooled to 0—5°C. and 15 parts of 36 Tw hydrochloric acid
added. The mixture is then tetrazotised by addition of 3.46 parts of sodium nitrite in
25 parts of water. The tetrazo suspension is then added to a suspension of 9.8 parts
of 1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one in 75 parts of water at
0—5°C. and pH 7.0. The mixture is stirred at 0—5°C. for 4 hours, the pH being
maintained at 6—7 by addition of 2N sodium carbonate solution, and is finally stirred
35 at 20°C. for 16 hours. The dyestuff is precipitated by addition of potassium chloride,
collected by filtration and washed with 50 parts of a saturated solution of potassium
chloride. After drying in vacuo at 40°C., the dyestuff is found to contain 1.7 mols of
hydrolysable chlorine per mol of dye.

When applied to cellulose the dyestuff gives bright yellow shades of good fastness
to washing and light.

EXAMPLES 155—161

40 Similar dyestuffs are obtained if the 4,4'-diamino-diphenylurea-2,2'-disulphonic
acid used in Example 154 is replaced by an equivalent quantity of (Example 155)
4,4'-diaminostilbene-2,2'-disulphonic acid, (Example 156) 4,4'-diaminodiphenoxy-
ethane-2,2'-disulphonic acid, or (Example 157) benzidine-2,2'-disulphonic acid, or
45 (Examples 158—161 respectively) by coupling the tetrazonium salts from the con-
densation products of any of these diamines with 2 moles of cyanuric chloride and
1,3-phenylene diamine-4,6-disulphonic acid with 2,6-dihydroxyisonicotinic acid.

EXAMPLES 162—165

50 If the 1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one used in Example
154 is replaced by 7.65 parts of 1-ethyl-4-methyl-6-hydroxypyrid-2-one, a similar
dyestuff is obtained. Similar dyestuffs are also obtained if at the same time, the 4,4'-
diaminodiphenylurea-2,2'-disulphonic acid is replaced by 4.63 parts of 4,4'-diamino-
stilbene-2,2'-disulphonic acid (Example 163), or 5.01 parts of 4,4'-diaminodiphenoxy-
ethane-2,2'-disulphonic acid (Example 164) or by 4.3 parts of benzidine-2,2'-
55 disulphonic acid (Example 165).

EXAMPLES 166—169

60 If the 1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one used in Example
154 is replaced by 9.0 parts of 3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine, a
similar dyestuff is obtained. Other similar dyestuffs are obtained if at the same time
the 4,4'-diaminodiphenylurea-2,2'-disulphonic acid is replaced by 4.63 parts of 4,4'-
diaminostilbene-2,2'-disulphonic acid (Example 167) or 5.01 parts of 4,4'-diamino-

diphenoxyethane-2,2'-disulphonic acid (Example 168) or by 4.3 parts of benzidine-2,2'-disulphonic acid (Example 169).

EXAMPLE 170

To a suspension prepared by adding a solution of 10 parts of cyanuric chloride in 30 parts of acetone to a mixture of 75 parts of ice and 75 parts of water is added dropwise during 15 minutes a solution of 12.7 parts of aniline-2,5-disulphonic acid in 100 parts of water at pH 6.5. The mixture is stirred at 0—5°C. keeping the pH at 6—7 by addition of 2N sodium carbonate solution as required, for 2 hours.

A suspension of 9.65 parts of N-β-aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one is stirred at 40°C. and dissolved by addition of 2N sodium carbonate solution until solution is just complete. The pH of the solution is then adjusted to 7.5 with 2N hydrochloric acid and the solution added to the solution prepared as described in paragraph one. The solution is then stirred at 35—40°C. for 3 hours, keeping the pH at 7—8, by addition of 2N sodium carbonate solution as required.

A solution of 12.7 parts of aniline-2,5-disulphonic acid in 150 parts of water and 10 parts of hydrochloric acid (36° Tw) is diazotised at 0—5°C. by the gradual addition of 2N sodium nitrite solution until a faint excess of nitrous acid persists. The excess of nitrous acid is removed by addition of a 10% aqueous solution of sulphamic acid, and the solution is added to the coupling solution prepared as described in paragraph two. The mixture is stirred at 10°C. for 3 hours, keeping the pH at 6 by addition of 2N sodium carbonate solution as required, and the dyestuff is precipitated by addition of potassium chloride. The dyestuff is dried at 40°C.

When applied to cellulose it gives greenish yellow shades which are fast to washing treatments and to light.

The N-β-aminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one used in the above example can be obtained as follows:

A solution of 180 parts of ethylenediamine in 100 parts of water at 20—25°C. is added to a stirred mixture of 65 parts of acetoacetic ester and 56.5 parts of cyanoacetic ester at 20°C. The temperature is allowed to rise to 50—55°C. without external cooling, and when the heat of reaction begins to subside, the mixture is heated at 50±2°C. for 15—20 hours. The solution is then evaporated in vacuo at 80°C. for 2 hours to remove unchanged starting materials and the residue is dissolved in 400 parts of water. The cooled solution is then acidified with 115 parts of hydrochloric acid (36°Tw) until weakly acid to Congo red. After stirring at below 10°C. for several hours, the product is collected by filtration, washed with 200 parts of cold water and dried.

The product (46.1 parts) decomposes on melting at 265°C. and on analysis is found to contain C, 53.4; H, 5.4; N, 20.7; C₆H₁₁O₂N₃.H₂O requires C, 53.45; H, 5.95; N, 20.8.

The following table describes further examples of the invention obtained in similar manner by condensing the pyridone or pyridine compound named in column I with the chloro compound named in column II and coupling the resultant product with the diazonium salt of the amine named in column III.

	I	II	III	Shade
171	1-(β -aminoethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(2',5'-disulphoanilino)-s-triazine	<i>m</i> - β -sulphatoethyl-sulphonylaniline	greenish yellow
172	— do —	— do —	<i>p</i> - β -sulphatoethylsulphonylaniline	— do —
173	— do —	— do —	2-methoxy-5-(β -sulphatoethyl sulphonyl)aniline	— do —
174	— do —	— do —	2-methoxy-5-methyl-4-(β -sulphatoethyl sulphonyl) aniline	— do —
175	— do —	2,4-dichloro-6-(<i>m</i> -sulphoanilino)-s-triazine	— do —	— do —
176	— do	2,4-dichloro-6-(<i>m</i> - β -sulphatoethyl sulphonylanilino)-s-triazine	aniline-2,5-disulphonic acid	yellow
177	— do —	2,4-dichloro-6-(<i>N</i> - α -sulphomethyl-anilino)-s-triazine	— do —	— do —
178	— do —	— do —	2-aminonaphthalene-3,6,8-trisulphonic acid	reddish yellow
179	1- β -aminoethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —	aniline-2,5-disulphonic acid	greenish yellow

	I	II	III	Shade
180	1- β -aminoethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(3',5'-disulphoanilino)-s-triazine	2-methoxy-5- β -sulphatoethylsulphonyl-aniline	greenish yellow
181	— do —	— do —	orthanilic acid	— do —
182	— do —	2,4-dichloro-6-(3'- β -sulphatoethylsulphonylanilino)-s-triazine	— do —	— do —
183	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	2-chloro-4-(3'-amino-4'-sulphoanilino)-6-(2'-methyl-5'-sulphoanilino)-s-triazine	— do —
184	— do —	2,4-dichloro-6-(3'-sulphoanilino)-s-triazine	2-chloro-4-(3'-amino-4'-sulphoanilino)-6-(<i>m</i> -sulphoanilino)-s-triazine	— do —
185	— do —	— do —	2-chloro-4(<i>m</i> -sulphoanilino)-6-(5'-amino-2',4'-disulphoanilino)-s-triazine	— do —
186	— do —	2,4-dichloro-6-(3'- β -sulphatoethylsulphonylanilino)-s-triazine	2-chloro-4-(3'- β -sulphatoethylsulphonylanilino)6-(5'-amino-2',4'-disulphoanilino)-s-triazine	— do —
187	— do —	2,4-dichloro-6-(N- ω -sulphomethylanilino)-s-triazine	2-chloro-4-(N- ω -sulphomethyl-anilino)-6-(5'-amino-2',4'-disulphoanilino)-s-triazine	— do —

	I	II	III	Shade
188	1-β-aminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(N-ω-sulphomethyl-anilino)-s-triazine	2-chloro-4-(N-ω-8-sulphomethyl-anilino)-6-(4'-amino-2',5'-disulpho-anilino)-s-triazine	reddish yellow
189	— do —	2,4-dichloro-6-(p-sulphoanilino)-s-triazine	2-chloro-4-(p-sulphoanilino)-6-(5'-amino-2',4'-disulphoanilino)-s-triazine	greenish yellow
190	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	2-chloro-4-(2'-methyl-5'-sulphoanilino)-6-(4'-amino-2',5'-disulphoanilino)-s-triazine	reddish yellow
191	1-β-aminoethyl-3-cyano-4-carboxyethyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(m-sulphoanilino)-s-triazine	2-chloro-4-(m-sulphoanilino)-6-(4'-amino-2',5'-disulphoanilino)-s-triazine	— do —
192	1-β-aminoethyl-3-carboxy-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	— do —
193	1-β-methylaminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(2',5'-disulphoanilino)-s-triazine	2-chloro-4-(2',5'-disulphoanilino)-6-(4'-amino-2',5'-disulphoanilino)-s-triazine	— do —
194	1-β-phenylaminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	— do —	— do —	— do —
195	1-β-ethylaminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	— do —	— do —	— do —
196	1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(2',5'-disulphoanilino)-s-triazine	metanilic acid	greenish yellow
197	— do —	— do —	sulphanilic acid	— do —
198	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	2-chloro-4-(2'-methyl-5'-sulphoanilino)-6-(4'-amino-2',5'-disulphoanilino)-s-triazine	reddish yellow
199	1-(4'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	— do —

The 1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one mentioned in the table can be prepared as follows. To a solution of sodium ethoxide in absolute ethanol prepared by adding 12.7 parts of sodium to 250 parts of absolute ethanol is added 55.5 parts of ethyl cyanoacetate and 111 parts of 3-nitroacetoacetanilide in 250 parts of absolute ethanol. The mixture is stirred and refluxed for 16 hours then cooled to 5° and 50 parts of hydrochloric acid (36°Tw) are added. The precipitated 1-(3'-nitrophenyl)-3-cyano-4-methyl-6-hydroxy-pyrid-2-one is filtered, washed with water and then with acetone and dried at 60°. The product (87 parts) decomposes above 300°C. and on analysis is found to contain C, 57.8; H, 3.0; N, 15.0% and give a molecular ion at 271. $C_{15}H_9N_3O_4$ requires C, 57.6; H, 3.3; N, 15.4% molecular weight 271.

A mixture of 27.1 parts the above product dissolved in 600 parts of water by the addition of just sufficient sodium hydroxide solution just to cause complete solution and 10 parts of 3% palladium on charcoal catalyst is hydrogenated at atmospheric pressure and 20°C. until the rapid absorption of hydrogen is complete. The mixture is filtered and the filtrate is acidified until just acid to congo red by the addition of hydrochloric acid (36°Tw). After standing at 20°C. for several days the product is collected by filtration, washed with water and then acetone and dried.

The product (20.5 g) decomposes when heated above 300°C. and when analysed is found to contain C, 65.1; H, 4.2; N, 17.2% molecular ion 241. $C_{13}H_{11}N_3O_2$ requires C, 64.7; H, 4.6; N, 17.4% molecular weight 241.

The 1-(4'-aminophenyl) and 1-(3'-amino-4'-methylphenyl) compounds can be obtained in an analogous manner by starting from *p*-nitroacetoacetanilide or 5-nitro-4-methylacetoacetanilide instead of *m*-nitroacetanilide.

The 1-(β -aminoethyl)-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one can be obtained by heating the corresponding 3-cyano compound in 100% sulphuric at 50°C. for 24 hours, drowning out the reaction mixture, partially neutralising with potassium carbonate and extraction of the resulting precipitate with ethanol. It is obtained in the form of the sulphate.

EXAMPLE 200

The diazo component obtained by reacting 18.5 parts of cyanuric chloride with 26.8 parts of 1,4-phenylenediamine-3,6-disulphonic acid at 0—5°C./pH 3.5—5.0 and 17.3 parts of metanilic acid is diazotised and coupled with 13.7 parts of 2-methoxy-5-methylaniline in the presence of sodium acetate. The amina azo compound so obtained is diazotised and coupled with 17.8 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one to give a bis-azo dyestuff dyeing cotton and viscose rayon in bluish-red shades having excellent fastness to washing and to light.

The following table describes further examples obtained in similar manner to Example 200. One mole of the diamine in Column II is condensed with one mol of the acylating agent in Column III, and, where described, the product is then condensed with a further equivalent of the compound described in Column IV. The product is then diazotised and coupled with the coupling component described in Column V. The aminoazo compound so formed is diazotised and coupled with the pyridone coupling component described in Column VI to form a dis-azo dyestuff. The shades obtained when applied to cellulose are described in Column VII.

Example No.	II	III	IV	V	VI	VII
201	1,4-phenylenediamine-2,5-disulphonic acid	cyanuric chloride	—	1-aminonaphthalene-6-sulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	bluish red
202	— do —	— do —	—	1-aminonaphthalene-7-sulphonic acid	— do —	— do —
203	— do —	— do —	—	— do —	1-ethyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
204	— do —	— do —	—	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —
205	— do —	— do —	—	1-aminonaphthalene-6-sulphonic acid	— do —	— do —
206	— do —	— do —	—	— do —	1-ethyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
207	— do —	— do —	metanilic acid	— do —	— do —	— do —
208	1,3-phenylenediamine-4,6-disulphonic acid	— do —	— do —	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
209	— do —	— do —	—	— do —	— do —	— do —

No.	II	III	IV	V	VI	VII
210	1,3-phenylenediamine-4,6-disulphonic acid	tetrachloro-pyrimidine	—	1-aminonaphthalene-6-sulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	bluish red
211	— do —	2-methylsulphonyl-6-methyl-4,5-dichloro-pyrimidine	—	— do —	— do —	— do —
212	— do —	cyanuric chloride	4-β-sulphato-ethyl sulphonyl-aniline	— do —	— do —	— do —
213	— do —	2,4-dichloro-6-methoxy-s-triazine	—	— do —	— do —	— do —
214	— do —	cyanuric chloride	ammonia	— do —	— do —	— do —
215	— do —	— do —	metanilic acid	— do —	— do —	— do —
216	— do —	— do —	—	1-aminonaphthalene-7-sulphonic acid	— do —	— do —
217	— do —	— do —	4-sulphophenol	1-aminonaphthalene-6-sulphonic acid	— do —	— do —
218	— do —	— do —	—	— do —	1-ethyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —
219	— do —	— do —	—	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —

Example No.	II	III	IV	V	VI	VII
220	1,3-phenylenediamine-4,6-disulphonic acid	cyanuric chloride	—	1-aminonaphthalene 6-sulphonic acid	4-methyl-2,6-dihydroxypyridine	bluish red
221	1,3-phenylenediamine-6-sulphonic acid	— do —	metanilic acid	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
222	— do —	— do —	— do —	— do —	1-γ-methoxy-propyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
223	1,4-phenylenediamine-6-sulphonic acid	— do —	1-naphthylamine-3,6,8-trisulphonic acid	— do —	— do —	— do —
224	— do —	— do —	4-sulphophenol	— do —	— do —	— do —
225	1,3-phenylenediamine-4,6-disulphonic acid	— do —	—	cresidine	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —
226	— do —	— do —	—	2,5-dimethoxyaniline	— do —	— do —
227	— do —	— do —	sulphanilic acid	— do —	— do —	— do —
228	— do —	— do —	—	— do —	— do —	— do —

EXAMPLE 229

To a suspension prepared by adding a solution of 10 parts of cyanuric chloride in 30 parts of acetone to a mixture of 75 parts of ice and 75 parts of water is added dropwise during 15 minutes a solution of 12.7 parts of aniline-2,5-disulphonic acid in 100 parts of water at pH 6.5. The mixture is stirred at 0—5°C., keeping the pH at 6—7 by addition of 2N sodium carbonate solution as required, for 2 hours.

A suspension of 12.05 parts of 1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one is stirred at 40°C. in 200 parts of water at pH 6.5. The solution from paragraph 1 is added and the mixture is stirred at 40°C. for 5 hours keeping the pH at 6—7 by addition of 2N sodium carbonate solution as required. When acylation is complete, the solution is cooled to 5°C.

A suspension of 38.3 parts of 2-aminonaphthalene-3:6:8-trisulphonic acid in 150 parts of water and 25 parts of hydrochloric acid (36°Tw) is diazotised at 0—5°C. by the dropwise addition of 50 parts of 2N sodium nitrite solution until a faint excess of nitrous acid persists. Slight excess of nitrous acid is removed by addition of 10% sulphamic acid solution and the diazo suspension is then added to a solution of 13.7 parts of 2-methoxy-4-methyl-aniline in 100 parts of water and 12 parts of hydrochloric acid (36°Tw) at 10°C. The mixture is stirred for 5 hours at 10°C. and then at 20°C. for a further 18 hours. The monoazo compound is isolated by adding sodium chloride (10% weight/volume), filtering, and drying the precipitate at 60°C.

To a solution of 26.4 parts of the monoazo compound in 300 parts of water at 5°C. and pH 7.0 is added a solution of 3.45 parts of sodium nitrite in 25 parts of water. The solution is then added to a rapidly stirred mixture of 100 parts of crushed ice and 25 parts of hydrochloric acid (36°Tw) and the mixture stirred at 0—5°C. for 1 hour. Slight excess of nitrous acid is removed by addition of 10% sulphamic acid solution as required, and the diazotised monoazo is then added to the solution of the coupling component prepared as described in paragraph two. The mixture is stirred at 5°C. for 6 hours maintaining the pH at 6—7 by addition of 2N sodium carbonate as required.

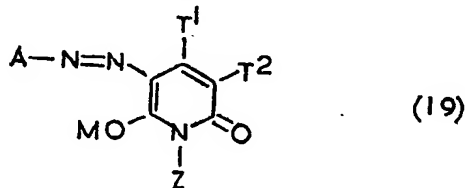
The dyestuff is precipitated by addition of potassium chloride, filtered, and dried at 40°C. When applied to cellulose it gives red shades which are fast to washing and to light.

In place of the 38.3 parts of 2-aminonaphthalene-3,6,8-trisulphonic used above there may be used (Example 230) 25.3 parts of aniline 2,5-disulphonic acid, (Example 231) 38.3 parts of 1-naphthylamine-2,5,7-trisulphonic acid, (Example 232) 30.3 parts of 2-naphthylamine-4,7-disulphonic acid, (Example 233) 30.3 parts of 2-naphthylamine-1,5-disulphonic acid, (Example 234) 41 parts of 1-aminobenzene-4-(2-chloro-4-methoxy-6-s-triazinylamino)-2,5-disulphonic acid or (Example 235) 41 parts of 1-aminobenzene-3-(2-chloro-4-methoxy-6-s-triazinylamino)-4,6-disulphonic acid when red dyestuffs similar in shade that described above are obtained with good fastness to washing and to light.

EXAMPLE 236

If in place of the 13.7 parts of 2-methoxy-4-methylaniline in Example 229 there are used 25.3 parts of 2-methoxy-1-aminonaphthalene-6-sulphonic acid there is obtained a dyestuff which gives dull violet shades when applied to cellulose with good fastness to washing and to light.

The invention also provides a process for the manufacture of the azo dyestuffs of the invention which contain the cellulose reactive group or groups attached through amino groups which comprises reacting an azo dyestuff of the formula:—



wherein A, M, T¹, T² and Z have the meanings stated above and which contains at least one amino or alkylamino group and at least one sulphonic acid group, with a reagent capable of condensing with the amino or alkylamino group and attaching thereto a residue containing a fibre-reactive group, e.g. carbyl sulphate or more especially a compound of the formula:—

X—halogen

wherein halogen is chlorine or bromine and X has the meaning stated, one molecular proportion of the reactant being used for each amino or alkylamino group present in the dyestuff.

5 This process of the invention can be conveniently carried out by stirring the azo dyestuff of formula (19) and the reactant together in water or in a mixture of water and a water-soluble organic liquid such as acetone, and gradually adding an acid binding agent such as sodium carbonate to neutralise the acid formed in the reaction. The resulting fibre-reactive dyestuff can then be isolated by conventional methods.

10 The said azo dyestuffs of formula (19) can themselves be obtained by diazotising an amine of the formula A—NH₂ and coupling the resulting diazo compound with a coupling component of formula 17, the amine and the coupling component together containing at least one amino or alkylamino group or a group such as a nitro group which is convertible to an amino group by methods other than alkaline hydrolysis. This last should be avoided since in general the pyridone ring, especially after coupling, is attacked by alkali. When it is desired to prepare metal complexes of the azo dyestuffs of the invention then it is preferred to prepare the metal complex of the corresponding dyestuff containing at least one amino or alkylamino group by treating the dyestuff with a solution of a metal compound, and subsequently reacting the metallised dyestuff containing an amino or alkylamino group or groups with a compound of the formula X-halogen.

Accordingly, the azo dyestuffs of formula (19) can be obtained by one of the following methods:—

25 (a) diazotising an aromatic diamine under conditions which lead to diazotisation of only one amino group, and coupling the resultant diazonium compound with a compound of formula (17) in which Z, T¹ and T² have the meanings stated in connection with formula (1)

(b) diazotising an aromatic amine, or tetrazotising an aromatic diamine and coupling the resultant diazonium or tetrazonium compound with a compound of formula (17) which contains an amino group.

30 (c) diazotising an aromatic amine or tetrazotising an aromatic diamine and coupling the resultant diazonium or tetrazonium compound with a compound of formula (17), either the amine or compound of formula (17) containing a nitro group, and then reducing the resultant azo compound to convert the nitro group to amino.

35 (d) Utilising as the amine or diamine in either of methods (b) and (c), one which contains a hydroxyl, carboxyl or methoxy group *ortho* to the diazotisable amino group, and subjecting the azo dyestuff to a treatment with a metallising agent to form the metal complex.

40 As examples of diamines which may be used in connection with process (a), there may be mentioned:

1,3-phenylene-diamine-4,6-disulphonic acid and
1,4-phenylene-diamine-2,5-disulphonic acid.

As examples of aromatic amines or diamines which may be used in connection with process (b) there may be mentioned:

45 aniline-2-, -3- and -4-sulphonic acids,

aniline-2, 4-, -2,5- and -3,5-disulphonic acids,

4-aminoacetanilide-3-sulphonic acid,

4-methoxyaniline-2-sulphonic acid,

1-naphthylamine-3-, -4-, -5-, -6-, -7- and -8-sulphonic acids,

50 2-naphthylamine-1-, -5-, -6-, -7-, and -8-sulphonic acids,

1-naphthylamine-2,5,7- and -3,6,8-trisulphonic acids,

1-naphthylamine-2,7-, -3,6-, -3,8-, -4,6- and -4,7-disulphonic acids,

2-naphthylamine-1,5-, -3,7-, -4,8-, -5,7- and -6,8-disulphonic acids,

2-naphthylamine-3,6,8-trisulphonic acid,

55 4-amino-phenol-2-carboxylic acid,

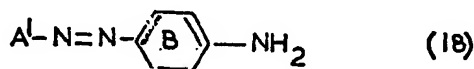
benzidine-2,2'-disulphonic acid,

4,4'-diaminodiphenylurea-2,2'-disulphonic acid,

4,4'-diaminostilbene-2,2'-disulphonic acid

and 4,4'-diaminodiphenoxyethane-2,2'-disulphonic acid.

60 Included within the scope of suitable amines are those of the formula:



wherein A^1 is an optionally substituted phenyl or naphthyl radical and the benzene ring B can contain substituents or form part of an optionally substituted naphthalene ring. As specific examples of such amines there may be mentioned 4-(2':5-disulphophenylazo)aniline and 4-(*p*-sulphophenylazo)-1-naphthylamine-6- or 7-sulphonic acid.

As examples of amines which can be used in connection with process (b) or process (c), there may be mentioned:

4-nitro-aniline-2-sulphonic acid,
4-nitro-4'-aminostilbene-2,2'-disulphonic acid,
and 4-(4'-nitro-2'-sulphophenylazo)-3-methylaniline.

As examples of amines which can be used in connection with process (b) or process (d) there may be mentioned:

2-aminophenol-4- and -6-sulphonic acids,
4-chloro-2-aminophenol-6-sulphonic acid,
6-chloro-2-aminophenol-4-sulphonic acid,
2-aminophenol-4,6-disulphonic acid,
anthranilic acid,
4- and 5-sulpho-2-aminobenzoic acids,
4-(2',5'-disulphophenylazo)-2,5-dimethoxyaniline.

As examples of amines which can be used in connection with processes (b), (c) or (d), there may be mentioned:

4-nitro-2-aminophenol-6-sulphonic acid,
6-nitro-2-aminophenol-4-sulphonic acid,
4- and 5-nitro-2-aminobenzoic acids.

As examples of coupling components which can be used in connection with process (a), (c) or (d) there may be mentioned:

2:6-dihydropyridine, 2:6-dihydroxy-3-cyano-4-methyl-pyridine, 1-(methyl or ethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one, 1-(β -hydroxyethyl or γ -methoxypropyl)-3-cyano-4-(methyl, phenyl or ethyl)-6-hydroxypyrid-2-one, 1-(phenyl, *p*-tolyl or *p*-anisyl)-3-cyano-4-(methyl or phenyl)-6-hydroxypyrid-2-one, 1-phenyl-3-(aminocarbonyl, carboxy or ethoxycarbonyl)-4-(methyl or phenyl)-6-hydroxypyrid-2-one, 2:6 - dihydroxy - 3 - (aminocarbonyl, ethoxycarbonyl, diethylaminocarbonyl) - 4-methylpyridine, 2:6 - dihydroxy - 3 - (aminocarbonyl or ethoxycarbonyl)pyridine, 2:6 - dihydroxy - 3 - aminocarbonyl - 4 - phenyl pyridine, 2:6 - dihydroxy - 3 - cyano - 4 - (carboxy, methoxycarbonyl or ethoxycarbonyl)pyridine, ethyl 2:6-dihydroxy-3-cyanopyrid-4-ylacetate, 2:6 - dihydroxy - 3 - cyanopyrid - 4 - ylacetamide, 2:6 - dihydroxy-3:4 - di(carboxy or ethoxycarbonyl)pyridine, 2:6 - dihydroxy - 3 - aminocarbonyl - 4 - ethoxycarbonylpyridine, 2:6 - dihydroxy - 4 - methylpyridine, ethyl 2:6 - dihydroxy - iso-nicotinate, 2:6 - dihydroxy - isonicotinamide, 2:6 - dihydroxy - iso - nicotinic acid diethylamide, 2:6 - dihydroxy - 4 - cyanopyridine, 2:6 - dihydroxy - 4 - phenylpyridine, 2:6 - dihydroxy - 4 - (*p* - hydroxyphenyl)pyridine, 2:6 - dihydroxy - 4 - (*p* - methoxyphenyl)pyridine, 2:4:6 - trihydroxypyridine and 2:6-dihydroxy-3-cyano-4-ethoxycarbonylmethylpyridine.

As examples of coupling components which may be used in connection with process (a) to (d) there may be mentioned:

1 - β - aminoethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - amino - ethyl - 3 - cyano - 4 - phenyl - 6 - hydroxypyrid - 2 - one, 1 - γ - aminopropyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - (β - aminoethyl)-3 - carboxy - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - aminoethoxyethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - aminopropyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - aminopropyl - 3 - cyano - 4 - phenyl - 6 - hydroxypyrid - 2 - one, 1 - (N - aminoethylamino)ethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - (β - aminoethyl) - 3 - cyano - 4 - ethoxycarbonyl - 6 - hydroxypyrid - 2 - one, 1 - (β - aminoethyl) - 3 - cyano - 4 - cyclohexyl - 6 - hydroxypyrid - 2 - one, 1 - (β - aminoethyl) - 3 - cyano - 4 - (3' - pyridyl) - 6 - hydroxypyrid - 2 - one, 1 - (β - aminopropyl) - 3 - cyano - 4 - dimethylaminocarbonyl - 6 - hydroxypyrid - 2 - one, 1 - β - methylaminoethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - phenylaminoethyl - 3 - cyano - 4 - methyl - 6 - hydroxypyrid - 2 - one, 1 - β - ethylaminoethyl - 3 - cyano - 4 - methyl -

5 6 - hydroxypyrid - 2 - one, 1 - β - aminoethyl - 4 - methyl - 3 - aminocarbonyl - 6 - hydroxypyrid - 2 - one, 1 - (3' - and 4' - aminophenyl) - 4 - methyl - 3 - aminocarbonyl - 6 - hydroxypyrid - 2 - ones, 1 - (3' - and 4' - aminophenyl) - 4 - methyl - 3 - cyano - 6 - hydroxypyrid - 2 - ones, 1 - (3' - amino - 4' - methylphenyl) - 3 - cyano - and - 3 - aminocarbonyl - 4 - methyl - 6 - hydroxypyrid - 2 - ones and 1 - (3' - amino - 4' - methoxyphenyl) - 3 - cyano - and - 3 - aminocarbonyl - 6 - hydroxypyrid - 2 - ones. 5

10 As examples of compounds of the formula X—halogen which can be reacted with the azo compounds of formula (19) there may be mentioned acryloyl chloride, β -chloropropionyl chloride, δ -bromopropionyl bromide, chloroacetyl chloride, α : β -dichloropropionyl chloride, 2:3-dichloroquinoxaline-5- or 6-carbonyl chloride, 2:3-dichloroquinazoline-5- or 6-sulphonyl chloride, 2:4-dichloroquinazoline-6 or 7-sulphonyl chloride, 2:4:6-trichloroquinazoline-7- or 8-sulphonyl chloride, 2:4:7- or 2:4:8-trichloroquinazoline-6-sulphonyl chloride, 2:4-dichloroquinazoline-6-carbonyl chloride, 2:4-dichloropyrimidine-5-carbonyl chloride, 2-methylsulphonyl-6-chloropyrimidine-4-carbonyl chloride, β -(4:5-dichloropyridazon-1-yl)-propionyl chloride, 1-(phenyl-4'-carbonyl chloride)-4:5-dichloro-6-pyridazone, 1-(phenyl-4'-chlorosulphonyl) - 4:5 - dichloro - 6 - pyridazone, 2:4:6 - trichloropyrimidine, 2:4:6-tri(chloro or bromo) - 5 - methyl, nitro- or cyanopyrimidine, tetra - fluoro-*cyclo* - butyl carbonyl chloride, trifluorocyclobutenecarbonyl chloride, β - (tetrafluorocyclobutyl)acryloyl chloride, β -trifluorocyclobutenyl) acryloyl chloride, 2:4:5:6-tetrachloropyrimidine, 2:4-dichloro-5-nitro-6-methylpyrimidine, 5-ethoxycarbonyl-2:4:6-trichloropyrimidine, 2:4:6-tribromopyrimidine, 2:4:6-trifluoropyrimidine, cyanuric chloride, cyanuric bromide, the primary condensation products of cyanuric chloride with ammonia, amines, organic hydroxy or mercapto compounds, such as 25 methanol, ethanol, phenol, α -naphthol, β -naphthol, chlorophenols cresols, sulphonated phenols, thiophenol, thioglycolic acid, methyl mercaptan, dimethyldithiocarbamic acid, 2-mercaptobenzthiazole, thioacetamide, primary alkylamines such as methylamine, ethylamine, *n*-propylamine, dimethylamine and diethylamine, β -hydroxy ethylamine, di(β -hydroxyethyl)amine, piperidine, morpholine, β -methoxyethylamine, aminoacetic acid, aniline, N-methylaniline, toluidine, anisidine, aniline-2:5-, 2:4- and 3:5-disulphonic acids, aniline-*o*-, *m*- and *p*-sulphonic acid, N-methylaniline *o*, *m*, and *p*-sulphonic acid, *o*-, *m*- and *p*-aminobenzoic acid, 4- and 5-sulpho-2-amino-35 benzoic acid, 2-aminotoluene-4-sulphonic acid, 5-amino-2-hydroxy-benzoic acid, β -aminoethane sulphonc acid, N-methylaminoethane sulphonc acid and mono- and disulphonic acids of 1-amino- and 2-amino-naphthalene. 35

The following examples in which parts are by weight are illustrative of the above method of manufacture:

EXAMPLE 237

40 A solution of 6.7 parts of 1,4-phenylenediamine-2,5-disulphonic acid in 100 parts of water and 10 parts of hydrochloric acid (36°Tw) at 0—5°C. is diazotised by the dropwise addition of 1.73 parts of sodium nitrite dissolved in 12.5 parts of water.

45 The diazonium solution so formed is then added to a stirred solution of 4.5 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in 250 parts of water at pH 7.0 and 0—5°C. The pH of the solution is maintained at 6—7 with 10% sodium carbonate solution as required and the mixture stirred at 0—5°C. for 5 hours. 45

50 To the solution is then added dropwise, a solution of 4.7 parts of cyanuric chloride in 30 parts of acetone and the mixture stirred at 0—5°C. for 2 hours maintaining the pH at 6—7 with 10% sodium carbonate solution as required. The dyestuff is precipitated by addition of sodium chloride and filtered off. The precipitate is intimately mixed with 1 part of anhydrous disodium hydrogen phosphate and 1.9 parts of anhydrous potassium dihydrogen phosphate, and dried at a temperature between 20°C. and 30°C. 50

55 When applied to cellulosic materials, the dyestuff obtained gives reddish yellow shades which are fast to washing and to light. 55

EXAMPLE 238

60 A solution of 6.7 parts of 1,3-phenylenediamine-4,6-disulphonic acid in 100 parts of water at 0—5°C. and pH 5.0 is added rapidly to a suspension prepared by dissolving 4.62 parts of cyanuric chloride in 15 parts of acetone and adding the resulting solution to 30 parts of water and 30 parts of ice. The mixture is stirred for 2 hours at 0—5°C. maintaining the pH at 4—5 by addition of 2N sodium carbonate solution. 60

The solution is then cooled to 0—5°C. and 7.5 parts of 36°Tw hydrochloric

acid added. The mixture is then diazotised by addition of 1.7 parts of sodium nitrite in 11.5 parts of water. The diazo suspension is then added to a suspension of 5.0 parts of 1- β -aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in 200 parts of water at pH 7.0 and 0—5°C. The mixture is stirred at 0—5°C. for 2 hours maintaining the pH at 7.0 by addition of 2N sodium carbonate solution, and is finally stirred for 16 hours gradually warming to 20°C.

A solution of 4.33 parts of sulphanilic acid in 50 parts of water at pH 6.5 is added dropwise to a suspension of 4.62 parts of cyanuric chloride in 15 parts of acetone, 50 parts of ice and 50 parts of water keeping the pH at 6—7 by addition of 2N sodium carbonate solution as required. The mixture is then stirred at 0—5°C. keeping pH at 6—7 with 2N Na₂CO₃ as required for 1½ hours. This solution so prepared is then added to the solution of azo dyestuff prepared in the preceding paragraph and the mixture is stirred and heated at 35—40°C. for 4 hours, the pH being maintained at 8—8.5 by adding 2N sodium carbonate solution.

The pH of the mixture was finally adjusted to 7.0 and the dyestuff precipitated by addition of sodium chloride. The dyestuff is dried at 40°C. and on analysis is found to contain 1.9 mols of hydrolysable chlorine per mol of dye.

When applied to cellulose the dyestuff gives greenish-yellow shades which have good fastness to washing treatments and to light.

Further examples of the invention are described in the following Table, being obtained by coupling the diazonium salt of the amine named in Column II with the coupling component in Column II and acylating the aminoazo compound so formed with sufficient of the acylating agent in Column IV to fully acylate the amino groups present in the molecule. Alternatively the diamines named in Column II can first be acylated with one equivalent of the acylating agent named in Column IV, this product is then diazotised and coupled with the coupling component in Column III and the product is then reacted with a further equivalent of the acylating agent in Column IV.

I Example	II Diazo Component	III Coupling Component	IV Acyating Agent	V Shade
239	1,4-phenylene diamine acid	1- β -aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(2'-methyl-5'-sulphophenylamino)-s-triazine	Reddish-Yellow
240	—ditto—	—ditto—	cyanuric chloride	—ditto—
241	—ditto—	—ditto—	2-methylsulphonyl-6-methyl-4,5-dichloropyrimidine	—ditto—
242	aniline-2,5-disulphonic acid	—ditto—	—ditto—	Yellow
243	2-aminonaphthalene-3,6,8-trisulphonic acid	—ditto—	—ditto—	Reddish-Yellow
244	—ditto—	1- β -aminoethyl-3-cyano-4-methyl-5-(2'-methoxy-5'-methylphenylazo)-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(2'-sulphophenylamino)-s-triazine	Red
245	—ditto—	—ditto—	tetrachloropyrimidine	—ditto—
246	—ditto—	1- β -aminopropyl-3-cyano-4-phenyl-6-hydroxypyrid-2-one	—ditto—	Reddish-yellow
247	1,4-phenylenediamine-2,5-disulphonic acid	1- β -aminoethyl-3-cyano-4-carboxyethyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(3'-sulphophenylamino)-s-triazine	—ditto—

I Example	II Diazo Component	III Coupling Component	IV Acyating Agent	V Shade
248	1,4-phenylene-diamine-2,5-disulphonic acid	1- β -aminoethyl-3-carboxy-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(3'-sulphophenylamino)-s-triazine	Reddish Yellow
249	—ditto—	1- β -methylaminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(2',5'-disulphophenylamino)-s-triazine	—ditto—
250	—ditto—	1- β -phenylaminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	—ditto—	—ditto—
251	—ditto—	1- β -ethylaminoethyl-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	—ditto—	—ditto—
252	3-(sulphate- β -hydroxyethylsulphonyl)-aniline	1- β -aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(2,5-disulphophenylamino)-s-triazine	greenish-yellow
253	4-(sulphate- β -hydroxyethylsulphonyl)-aniline	”	”	”
254	3-(sulphate- β -hydroxyethylsulphonyl)-6-methoxyaniline	”	”	”
255	3-methyl-4-(sulphate- β -hydroxyethylsulphonyl)-6-methoxyaniline	”	”	”
256	”	”	2,4-dichloro-6-(3-sulphophenylamino)-s-triazine	”
257	aniline-2,5-disulphonic acid	”	2,4-dichloro-6-(3- β -sulphatoethylsulphonylphenylamino)-s-triazine	Yellow

Example	Diazo Component	Coupling Component	Acyating Agent	Shade
258	aniline-2,5-disulphonic acid	1-(β -aminoethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(N- ω -sulphomethyl-anilino)-s-triazine	Yellow
259	"	"	carbaryl sulphate	"
260	1,4-phenylenediamine-2,5-disulphonic acid	"	"	reddish yellow
261	"	"	2,4-dichloro-6-(N- ω -sulphomethyl-anilino)-s-triazine	"
262	2-aminonaphthalene-3,6,8-trisulphonic acid	"	"	"
263	"	"	carbaryl sulphate	"
264	1,3-phenylene diamine-4,6-disulphonic acid	1-(β -aminoethyl)-3-amino-carbonyl-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(<i>p</i> -sulphoanilino)-s-triazine	greenish yellow

Example	Diazo Component	Coupling Component	Acylating Agent	Shade
265	1,3-phenylenediamine-4,6-disulphonic acid	1-(β -aminoethyl)-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	cyanuric chloride	greenish yellow
266	"	"	2,4-dichloro-6-methoxy-3-triazine	"
267	"	"	2,4-dichloro-6-(3'-sulphoanilino)-s-triazine	"
278	"	"	2,4-dichloro-6-(3'- β -sulphato-ethylsulphonylanilino)-s-triazine	"
269	"	"	carbonyl sulphate	"
270	"	"	2,4-dichloro-6-N- ω -sulphomethyl-methylanilino-s-triazine	"
271	aniline 2,5-disulphonic acid	"	"	"
272	3-(sulphato- β -hydroxyethylsulphonyl)-6-methoxy aniline	"	2,4-dichloro-6-(3,5-disulphoanilino)-s-triazine	"
273	1-aminobenzene-2-sulphonic acid	"	"	"
274	"	"	2,4-dichloro-6-(3'- β -sulphato-ethylsulphonylanilino)-s-triazine	"

Example	Diazo Component	Coupling Component	Acyating Agent	Shade
275	1,3-phenylenediamine-4-sulphonic acid	1-(β -aminoethyl)-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-(3'-sulphoanilino)-triazine	greenish yellow
276	"	"	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	"
277	1,4-phenylenediamine-2,5-disulphonic acid	1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine	reddish yellow
278	"	1-(4'-aminophenyl)-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	"	"
279	2-aminonapthalene-3,6,8-trisulphonic acid	"	cyauric chloride	yellow
280	"	"	2,4-dichloro-6-amino-s-triazine	"
281	"	1-(3'-amino-4-methylphenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	cyauric chloride	"
282	"	1-(3'-amino-5'-methoxyphenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	"	"
283	aniline-2,5-disulphonic acid	1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	2-methylsulphonyl-6-methyl-4,5-dichloropyrimidine	greenish methyl
284	"	"	tetrachloropyrimidine	"
285	aniline-3-sulphonic acid	1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6-(2',5'-disulphoanilino)-s-triazine	Greenish yellow
286	aniline-4-sulphonic acid	"	"	"
287	2-naphthylamine-3,6,8-trisulphonic acid	"	cyauric chloride	yellow

EXAMPLES 288—291

If the solution described in paragraph 1 of Example 238 is mixed with 4.2 parts of 4,4'-diaminodiphenylurea-2,2'-disulphonic acid and heated at 30—35°C. at pH 6.5, reaction takes place to provide a solution of bis-4-[2'-chloro-4'-(5''-amino-2'',4'' - disulphoanilino) - s - triazinylamino]diphenylurea - 2,2' - disulphonic acid. On tetrazotisation, coupling with 1-β-aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one and finally condensing with the reaction product of cyanuric chloride and sulphanilic acid in similar manner to Example 238, there is obtained a disazo dyestuff which gives greenish-yellow shades which have good fastness to washing treatments and to light. Dyestuffs similar in shade are also obtained if the 4,4'-diaminodiphenylurea-2,2'-disulphonic acid is replaced by an equivalent quantity of (Example 289) 4,4'-diaminostilbene - 2,2' - disulphonic acid, (Example 290) 4,4' - diaminodiphenoxyethane-2,2'-disulphonic acid, or (Example 291) benzidine-2,2'-disulphonic acid.

EXAMPLE 292

A mixture of 9.36 parts of 6-nitro-2-aminophenol-4-sulphonic acid, 100 parts of water and 12 parts of hydrochloric acid (36°Tw) is stirred at 0—5°C. and 2N sodium nitrite solution is added until a faint excess of nitrous acid persists. The excess of nitrous acid is removed by addition of 10% aqueous solution of sulphamic acid and the resultant suspension is added to a solution prepared by adding sodium hydroxide solution (40%) to a suspension of 8.1 parts of 1-β-aminoethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one (prepared as described above) and 16.5 parts of sodium acetate crystals, in 100 parts of water until solution is just complete.

The mixture is stirred at 10°C. for 4 hours and the precipitate is filtered off and washed with a 10% aqueous solution of sodium chloride.

A mixture of 5.48 parts of the monoazo compound so obtained, 150 parts of water, 2 parts of chromium acetate and 1 part of sodium acetate crystals is stirred and refluxed for 3 hours when formation of the 1:2-chromium complex is complete. The mixture is cooled to room temperature and the suspension is poured into 300 parts of a saturated aqueous solution of sodium chloride. The precipitated chromium complex is filtered off and washed with a 20% aqueous solution of sodium chloride.

To a suspension prepared by adding a solution of 24 parts of cyanuric chloride in 30 parts of acetone to 150 parts of ice/water is added a solution of 2.3 parts of 1-aminobenzene-3-sulphonic acid at pH 6.5 and the mixture is stirred at 0—4°C. keeping pH at 6—7 by simultaneous addition of 2N. sodium carbonate solutions as required. When the condensation is complete, the resultant solution is added to a suspension of 11.6 parts of the 1:2-chromium complex prepared as described above and the mixture is stirred at 35—40°C. for 4 hours maintaining the pH at 8—9 by addition of sodium carbonate as required. The solution is then cooled to 20°C., the pH adjusted to 6.5 and the dye precipitated by addition of sodium chloride. The dye is dried at 40°C. under vacuum and on analysis is found to contain 2.05 atoms of hydrolysable chlorine per mol. of dye.

When applied to cellulose the dye gives unusually bright bluish red shades with good fastness to washing and to light.

Further Examples of the invention are illustrated in the following Table, being obtained by forming the metal complex of the aminoazo compound stated in Columns II and III, forming the symmetrical 2:1 complex in the case of chromium and cobalt and the 1:1-complex in the case of copper, and this metallised azo compound being then condensed with the acylating agent indicated in Column IV.

I Example	II Dyebase	III Metal	IV Acyating Agent	V Shade
293	1- β -aminoethyl-3-cyano-4-methyl-5-(2'-hydroxy-3'-chloro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	Cr	2,4-dichloro-6-(3'-sulphophenylamino)-s-triazine	Reddish-Orange
294	— do —	"	2,4,5,6-tetrachloropyrimidine	— do —
295	— do —	"	acryloyl chloride	— do —
296	— do —	"	2,4-dichloroquinazoline-5-carbonyl chloride	— do —
297	— do —	"	2,4-dichloropyrimidine-5-carbonylchloride	— do —
298	— do —	"	2,3-dichloroquinoxaline-6-carbonyl chloride	— do —
299	— do —	"	2-(phenyl-4'-carbonylchloride)-4,5-dichloro-6-pyridazone	— do —
300	— do —	Co	2,4,6-trichloro-5-cyanopyrimidine	Orange
301	— do —	"	2,4-dichloro-6-(N-methylamino)-s-triazine	— do —
302	— do —	"	2,4-dichloro-6-(2,5-disulphophenylamino)-s-triazine	— do —
303	1- β -aminopropyl-3-cyano-4-methyl-5-(2'-hydroxy-3,5'-disulphophenylazo)-6-hydroxypyrid-2-one	Co	cyanuric chloride	Orange

I Example	II Dyebase	III Metal	IV Acylating Agent	V Shade
304	1-β-aminopropyl-3-cyano-4-carboxyethyl-5-(2'-hydroxy-3'-nitro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	Cr	2,4-dichloro-6-methoxy-s-triazine	bluish-red
305	— do —	Cr	2,4-dichloro-6-phenoxy-s-triazine	— do —
306	— do —	”	2,4-dichloro-6-(2'-methyl-5'-sulphophenylamino)-s-triazine	— do —
307	— do —	Cu	— do —	Orange
308	— do —	”	— do —	Orange
309	1-β-aminoethyl-3-cyano-4-methyl-2'-hydroxy-4'-(2''-naphthylazo-3'',6'',8'',-trisulphonic acid)-5'-methylphenylazo]-6-hydroxyl-pyrid-2-one	”	Acryloyl chloride	— do —
310	1-β-aminoethyl-3-cyano-4-methyl-5(2'-hydroxy-3'-nitro-5'-sulphophenylazo)-6-hydroxy-pyrid-2-one	”	2,4-dichloro-6-(3'-sulphophenylamino)-s-triazine	Reddish-black
311	1-(4'-aminophenyl)-3-cyano-4-methyl-5-(3'-nitro-2'-hydroxy-5'-sulphophenylazo)-6-hydroxy-pyrid-2-one	Co	— do —	Orange
312	1-(4'-aminophenyl)-3-cyano-4-methyl-5-(3'-chloro-2'-hydroxy-5'-sulphophenylazo)-6-hydroxypyrid-2-one	Cr	— do —	red
		”	— do —	reddish-orange

I Example	II Dyebase	III Metal	IV Acyating Agent	V Shade
313	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-5'-sulphophenylazo)-6-hydroxy-pyrid-2-one	Cr	2:4-dichloro-6-(3'-sulphophenylamino)-s-triazine	reddish-orange
314	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-3',5'-disulphophenylazo)-6-hydroxypyrid-2-one	„		— do —
315	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-4'-sulphonaphth-1'-ylazo)-6-hydroxypyrid-2-one	„		bluish-red
316	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-6'-nitro-4'-sulphonaphth-1'-ylazo)-6-hydroxypyrid-2-one	„		— do —
317	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-3'-chloro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	„	— do —	Orange
318	1-(4'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-3'-chloro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	„	— do —	— do —
319	1-(3'-aminophenyl)-3-cyano-4-methyl-5-(2'-hydroxy-3'-nitro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	Cu	— do —	— do —
320	1-(β-aminoethyl)-3-aminocarbonyl-4-methyl-5-(2'-hydroxy-3'-nitro-5'-sulphophenylazo)-6-hydroxypyrid-2-one	Cr	— do —	red

I Example	II Dyebase	III Metal	IV Acylating Agent	V Shade
321	1-(β -aminoethyl)-3-aminocarbonyl-4-methyl-5-(2'-hydroxy-3'-nitro-5'-sulphophenylazo)-6-hydroxypyrid-2-1	Co	2:4-dichloro-6-(3'-sulphophenylamino)-s-triazine	Orange
322	— do —	Cu	— do —	reddish-yellow
323	1-(β -aminoethyl)-3-aminocarbonyl-4-methyl-5-(2'-hydroxy-3',5'-disulphophenylazo)-6-hydroxypyrid-2-one	Cr	— do —	yellowish-red
324	— do —	Co	— do —	Orange
325	1-(β -aminoethyl)-3-aminocarbonyl-4-methyl-5-[2'-hydroxy-5'-methyl-4'(3',6'',8'',-trisulphonaphth-2'',-ylazo)phenylazo]-6-hydroxypyrid-2-one	Cu	— do —	reddish-black

EXAMPLE 326

A mixture of 13.45 parts of 2-aminophenol-4,6-disulphonic acid, 100 parts of water and 15 parts of hydrochloric acid (36°Tw) is diazotised at 0—5°C. by the addition of 2N sodium nitrite solution until a slight excess is present. The excess of sodium nitrite is decomposed by the addition of a 10% aqueous solution of sulphamic acid, and the resulting solution is added to a solution of 12.05 parts of 1-(3'-amino-phenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one in 100 parts of water, in which it is dissolved by the addition of just sufficient sodium hydroxide solution to cause complete solution, and 5 parts of glacial acetic acid. The mixture is stirred at 5° for 5 hours and then the product is collected by filtration, washed with ice-cold water, and dried in vacuo at 40°C.

3.7 Parts of cobalt (II) sulphate are stirred and refluxed in 35 parts of water in an atmosphere of nitrogen for 15 minutes, and the solution is allowed to cool to 80°C. 6.8 parts of triethylenetetramine are added and the resulting solution is stirred and refluxed in an atmosphere of nitrogen for 15 minutes and then allowed to cool to 30°C. 2.5 Parts of sodium carbonate are added followed by 10.4 parts of the amino-azo compound of paragraph 1 and the mixture is stirred and refluxed for 5 minutes in an atmosphere of nitrogen and then cooled and stirred for 16 hours at 25°C. in an atmosphere of nitrogen. The product is collected by filtration and washed with cold water and dried in vacuo at 40°C.

A solution of 5.56 parts of aniline-2,5-disulphonic acid in 50 parts of water at

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- pH 6.5 is added to a suspension prepared by adding a solution of 5 parts of cyanuric chloride in 30 parts of acetone to a mixture of 50 parts of ice and 50 parts of water, and the resulting mixture is stirred at 0—5°C. for 2½ hours, the pH being maintained between 6 to 7 by the addition of sodium carbonate solution as necessary. A suspension of 7.25 parts of the cobalt complex of paragraph 2 in 75 parts of water is then added to the solution, and the mixture is stirred at 40°C. for 3 hours, the pH being maintained at 8.5 by the addition of sodium carbonate solution as necessary. The solution is then cooled to 10°C. and the dyestuff precipitated by adding potassium acetate, collected by filtration and washed with ethanol.
- The dyestuff so obtained is dried in vacuo at 40°C. and, when analysed, is found to contain 2.1 mols of hydrolysable chlorine for each mol of dye. When applied to cellulose it yields orange-brown shades of excellent fastness to light and also to washing.
- Further examples of the invention are illustrated in the following Table, being obtained by treating the symmetrical 2:1 cobalt complex of the ligand named in column IV with the azo compound formed by coupling the diazo component named in column II with the coupling component named in column III, and then acylating the resulting 1:2 unsymmetrical cobalt complex with the indicated amount of the acylating agent named in column IV so as completely to acylate all the amino groups in the complex.

Example	Diazo component	Coupling Component	Ligand	Acyating Agent	Shade
327	2-aminophenol-4-sulphonic acid	1-(4'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	triethylene tetramine	2,4-dichloro-6-(2',5'-disulpho-anilino)-s-triazine (2 moles)	Yellow-brown
328	2-aminophenol-4,6-disulphonic acid	— do —	— do —	— do —	— do —
329	2-amino-6-nitrophenol-4-sulphonic acid	— do —	— do —	— do —	Red-brown
330	— do —	1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	Red
331	— do —	2,6-dihydroxyisonicotinic acid	— do —	— do — (1 mole)	Brown-red
332	— do —	2,6-dihydroxy-nicotinic acid	— do —	— do —	— do —
333	— do —	1-ethyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	Red
334	— do —	3-ethoxycarbonyl-4-amino-2,6-dihydroxy pyridine	— do —	— do —	Yellow-brown
335	— do —	1-ethyl-3-cyano-4-phenyl-6-hydroxy-pyrid-2-one	— do —	— do —	Red

Example	Diazo Component	Coupling Component	Ligand	Acyating Agent	Shade
336	2-hydroxy-1-naphthylamine-4-sulphonic acid	2,6-dihydroxyisonicotinic acid	triethylene tetramine	2,4-dichloro-6-(2',5'-disulpho-anilino)-s-triazine (1 mole)	blue-red
337	2-hydroxy-6-nitro-1'-naphthylamine-4-sulphonic acid	— do —	— do —	— do —	reddish-black
338	2-aminophenol-4,6-disulphonic acid	1-(4'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	2,4-dichloro-6-(4'-sulphato-ethylsulphonylanilino)-s-triazine (2 moles)	yellow-brown
339	— do —	— do —	diethylene triamine	— do — (1 mole)	— do —
340	— do —	1-(β -aminoethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do — (1 mole)	— do —
341	— do —	— do —	triethylene tetramine	carbonyl sulphate (2 moles)	— do —
342	2-aminophenol-4-sulphonic acid	— do —	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoanilino)-s-triazine (2 moles)	— do —
343	— do —	— do —	— do —	2,4-dichloro-6-(3',6',8'-trisulphonaphth-2'-ylamino)-s-triazine (2 moles)	— do —

Example	Diazo Component	Coupling Component	Ligand	Acylating agent	Shade
344	2-aminophenol-4-sulphonic acid	1-(β -aminoethyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	diethylene triamine	2,4-dichloro-6-(3',6'-8'-tri-sulphonaphth-2'-ylamino)-s-triazine (1 mole)	yellow-brown
345	2-amino-6-nitrophenol-4-sulphonic acid	2,6-dihydroxyisonicotinic acid	triethylene tetramine	— do — (1 mole)	reddish brown
346	— do —	1,4-dimethyl-3-aminocarbonyl-hydroxy-pyrid-2-one	— do —	2,4-dichloro-6-(2',5'-disulpho-anilino)-s-triazine (1 mole)	red
347	— do —	1- β -hydroxyethyl-3-amino-carbonyl-4-phenyl-6-hydroxypyrid-2-one	— do —	— do — (1 mole)	— do —
348	— do —	1- β -aminoethyl-3-amino-carbonyl-4-methyl-6-hydroxypyrid-2-one	— do —	— do — (2 moles)	— do —
349	— do —	1-ethyl-3-N,N-dimethyl-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	— do —	— do — (1 mole)	— do —
350	— do —	1-(3'-methoxypropyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do — (1 mole)	— do —

Example	Diazo Component	Coupling Component	Ligand	Acylating Agent	Shade
351	2-amino-phenol-4-sulphonic acid	1-ethyl-3-cyano-4-(4'-methoxyphenyl)-6-hydroxypyrid-2-one	triethylene tetramine	2,4-dichloro-6-(2',5'-disulpho-anilino)-s-triazine (1 mole)	red
352	— do —	1-methyl-3-cyano-4-(3'-methylphenyl)-6-hydroxypyrid-2-one	— do —	— do — (1 mole)	— do —
353	— do —	4-methyl-2,6-dihydroxypyridine	— do —	— do — (1 mole)	— do —
354	— do —	3,4-dimethyl-2,6-dihydroxypyridine	— do —	— do — (1 mole)	— do —
355	2-amino-1-naphthol-4-sulphonic acid	2,6-dihydroxyisonicotinic acid	— do —	— do — (1 mole)	bluish-red
356	6-chloro-2-aminophenol-4-sulphonic acid	1-(3'-aminopropyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do — (2 moles)	reddish brown
357	— do —	1-(3'-aminopropyl)-3-cyano-4-(3'-methylphenyl)-6-hydroxypyrid-2-one	— do —	2,4-disulpho-6-(3'-sulpho-anilino)-s-triazine (2 moles)	— do —
358	— do —	1-(β-aminoethyl)-3-cyano-4-ethyl-6-hydroxypyrid-2-one	— do —	2,4-disulpho-6-(4'-sulpho-anilino)-s-triazine (2 moles)	— do —
359	6-chloro-2-aminophenol-4-sulphonic acid	1-(β-methylaminoethyl)-3-methyl-6-hydroxypyrid-2-one	triethylene tetramine	2,4-dichloro-6-(3'-sulpho-N-methylanilino)-s-triazine (2 moles)	reddish brown
360	— do —	— do —	— do —	2,4-dichloro-6-(4'-sulphophenoxy)-s-triazine	— do —
361	— do —	— do —	— do —	2,4-dichloro-6-(3',5'-disulphophenoxy)-s-triazine	— do —

EXAMPLE 362

- 5 9.3 parts of cyanuric chloride are condensed with 13.4 parts of 1,3-phenylene-diamine-4,6-disulphonic acid at 0—4°C./pH 4—5 and the dichloro-*s*-triazine compound is diazotised and coupled with 9.8 parts of 1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyridin-2-one in a similar manner to Example 238. 5
- 10 A solution of 9.4 parts of 1,3-phenylene-diamine-4-sulphonic acid in 150 parts of water is neutralised with dilute caustic soda solution and added, and the mixture is stirred at 30—40°C. and kept at pH 5—7 until one chlorine atom of the dichloro-*s*-triazine group has been replaced. 10
- 15 The solution is cooled to 0—4°C. and stirred vigorously and a solution of 9.3 parts of cyanuric chloride in 30 parts of acetone is added. The resultant mixture is stirred at 0—4°C. for 2 hours, keeping the pH at 5—7, then 650 parts of water are added, followed by 15 parts of a 1:2 mixture of disodium hydrogen phosphate and potassium dihydrogen phosphate and then 240 parts of sodium chloride. The precipitated dyestuff is filtered off, mixed with 6 parts of the mixture of phosphates and dried. 15
- 20 The product contains 3:0 hydrolysable chlorine atoms for each azo group and colours cellulose textile materials in bright greenish-yellow shades of excellent fastness to washing and light. 20
- Further examples, similar to Example 362 are set out in the following table, being obtained by condensing the diamine of column II with one mole of cyanuric chloride, diazotising and coupling with the pyridone compound of column III, reacting the resultant azo compound with the diamine of column IV and finally reacting with the heterocyclic compound of column V.

Example	II	III	IV	V	Shade
363	1,3-phenylene-diamine-4,6-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	1,4-phenylene-diamine-2-sulphonic acid	cyanuric chloride	greenish yellow
364	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	— do —	— do —
365	— do —	— do —	1,3-phenylene-diamine-4-sulphonic acid	2,4,6-trichloropyrimidine	— do —
366	— do —	— do —	— do —	2,4,5,6-tetrachloropyrimidine	— do —
367	— do —	— do —	1,3-phenylene-diamine-4,6-disulphonic acid	cyanuric chloride	— do —
368	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	— do —	— do —
369	— do —	— do —	1,4-phenylene-diamine-2-sulphonic acid	— do —	— do —
370	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	— do —	— do —
371	— do —	— do —	1,3-phenylene-diamine-4,6-disulphonic acid	— do —	— do —
372	— do —	1-ethyl-3-(ethylaminocarbonyl)-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	— do —	— do —
373	— do —	1-ethyl-3-(phenylaminocarbonyl)-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4,6-disulphonic acid	— do —	— do —

Example	II	III	IV	V	Shade
374	1,3-phenylene-diamine-4,6-disulphonic acid	1-ethyl-3-(N-methyl-N-benzyl-aminocarbonyl)-4-phenyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4,6-disulphonic acid	cyanuric chloride	greenish yellow
375	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	— do —
376	— do —	— do —	1,3-phenylene-diamine-4-sulphonic acid	— do —	— do —
377	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	— do —	— do —
378	— do —	— do —	1,3-phenylene-diamine-4-sulphonic acid	2,4-dichloro-6-methoxy-s-triazine	— do —
379	— do —	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	1,4-phenylene-diamine-2,5-disulphonic acid	2,4-dichloro-6-(4'-sulphophenoxy)-s-triazine	— do —
380	1,4-phenylene-diamine-2,5-disulphonic acid	1-(3'-methoxypropyl)-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	cyanuric chloride	reddish yellow
381	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	— do —

The invention also provides a process for manufacture of the new fibre-reactive azo dyestuffs of the invention which contain as the reactive group or groups one or more 1:3:5-triazine nuclei substituted by a chlorine atom and by an optionally substituted amino group by reacting the corresponding dyestuff containing at least one 1:3:5-triazine nucleus substituted by two chlorine atoms with ammonia or the appropriate primary or secondary amine under such conditions that one of the chlorine atoms attached to each 1:3:5-triazine nucleus is replaced by an optionally substituted amino group.

In general this replacement can be effected by heating a mixture of ammonia or the amine and the dyestuff in aqueous solution at from about 30 to about 60°C. and maintaining the pH of the solution at from 6 to 8 by addition of an alkali to neutralise the liberated hydrogen chloride as it is formed.

This process is illustrated by the following Examples in which parts are by weight:

EXAMPLE 382

A solution of the sodium salt of 26.8 parts of 1,4-diaminobenzene-2,5-disulphonic acid in 500 parts of water is mixed with 50 parts of 2N sodium nitrite solution and cooled to 0° to -3°C. 30 Parts of concentrated hydrochloric acid are then added and the diazonium salt is stirred for 30 minutes at 0°C. Any residual nitrous acid is destroyed by the addition of sulphamic acid. The diazonium chloride so obtained is added to a neutral solution of 17.8 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in 600 parts of water at 0-4°C. with stirring and the pH adjusted slowly to 7-7.5 until the coupling has been accomplished. The solution so obtained is mixed with 18.5 parts of powdered cyanuric chloride at 0-8°C. and the mixture stirred at pH 5-6 until the amino group of the azo-compound has completely reacted. The solution containing the dichloro-s-triazinyl dye is mixed with a solution of the sodium salt of 17.5 parts of sulphanilic acid in 200 parts of water and the mixture stirred at pH 5-6, at 30-40°C. until one chlorine atom of the dichloro-s-triazinyl dye has completely reacted. The dyestuff is precipitated by the addition of sodium chloride, filtered off and dried.

When applied to cotton and viscose rayon textile materials the dyestuff yields bright reddish-yellow shades having excellent fastness to wet treatments such as washing and to light.

EXAMPLE 383

In place of 26.8 parts of the diazo-component used in Example 382 there are used 26.8 parts of 1,3-diaminobenzene-4,6-disulphonic acid whereby a greenish-yellow dyestuff is obtained.

EXAMPLE 384

18.5 Parts of cyanuric chloride are condensed with 26.8 parts of 1,3-phenylenediamine-4,6-disulphonic acid at 0-4°C./pH 4.5 and the dichloro-s-triazinyl intermediate diazotised and coupled with 17.8 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in a similar manner to Example 238. The dichloro-s-triazinyl dyestuff so obtained is reacted with 13.4 parts of 1,4-phenylenediamine-2,5-disulphonic acid at 30-40°C./pH 5-7 until one chlorine atom from each of two moles of the dichloro-s-triazinyl dyestuff has completely reacted to give a bis-(monochloro-s-triazinyl)dye which is then isolated by the addition of sodium chloride.

The dyestuff dyed cotton and viscose rayon in bright greenish-yellow shades having excellent fastness to wet treatments such as washing and to light.

EXAMPLE 385

In place of the 13.4 parts of the 1,4-phenylene-diamine-2,5-disulphonic acid used in Example 384 there are used 20.1 parts of 4,4'-diamino-diphenylurea-2,2'-disulphonic acid whereby a similar dyestuff is obtained.

EXAMPLE 386

The dichloro-s-triazinyl dyestuff obtained by the diazotisation and coupling of the condensation product between 18.5 parts of cyanuric chloride and 26.8 parts of 1,3-phenylenediamine-4,6-disulphonic acid with 17.8 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one is reacted at 30-40°C./pH 5-7 with the condensation product obtained by reacting 18.5 parts of cyanuric chloride with 18.8 parts of 1,3-phenylenediamine-4-sulphonic acid and 17.3 parts of metanilic acid, until one chlorine atom of the dichloro-s-triazinyl dye has completely reacted. The bis-(monochloro-s-triazinyl)dye is isolated by the addition of sodium chloride. It dyes cotton

and viscose rayon in bright greenish-yellow shades having excellent fastness to washing and to light.

Further Examples, similar to that described in Example 386 can be obtained when the product of equimolar proportions of cyanuric chloride and the diamine of Column II is diazotised and coupled with the coupling component of Column III. The monoazo compound is then reacted with an equimolar proportion of the product of the condensation of 1 mole of the heterocyclic compound of Column IV and 1 mole of the diamine of Column V.

Example	II	III	IV	V	Shade
387	1,3-phenylene-diamine-4,6-disulphonic acid	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-amino-s-triazine	1,3-phenylene-diamine-4-sulphonic acid	greenish yellow
388	— do —	1-(3'-methoxy propyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one	— do —	— do —	— do —
389	— do —	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxy-pyrid-2-one	— do —	— do —	— do —
390	— do —	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoanilo)-s-triazine	— do —	— do —
391	— do —	— do —	2,4,6-trichloropyrimidine	— do —	— do —
392	— do —	— do —	2,4,5,6-tetrachloropyrimidine	— do —	— do —
393	— do —	— do —	2,4-dichloro-6-(3'-sulphoanilino)-s-triazine	1,4-phenylene-diamine-2-sulphonic acid	— do —
394	— do —	— do —	2,4-dichloro-6-amino-s-triazine	— do —	— do —
395	— do —	— do —	2,4-dichloro-6-β-hydroxyethylamino-s-triazine	1,4-phenylene-diamine-2,5-disulphonic acid	— do —
396	— do —	— do —	— do —	1,3-phenylene-diamine-4,6-disulphonic acid	— do —

Example	II	III	IV	V	Shade
397	1,3-phenylene-diamine-4-sulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxy-pyrid-2-one	2,4-dichloro-6- β -hydroxy-ethylamino- <i>s</i> -triazine	1,3-phenylene-diamine-4,6-disulphonic acid	greenish yellow
398	— do —	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	— do —
399	1,4-phenylene-diamine-2-sulphonic acid	— do —	— do —	— do —	yellow
400	— do —	3-aminocarbonyl-4-methyl-2,6-dihydroxypyridine	— do —	— do —	— do —
401	— do —	3-methylaminocarbonyl-4-methyl-2,6-dihydroxy pyridine	— do —	— do —	— do —
403	1,3-phenylene-diamine-4,6-disulphonic acid	1-ethyl-3-phenylamino-carbonyl-4-methyl-6-hydroxypyrid-2-one	2,4-dichloro-6-amino- <i>s</i> -triazine	1,3-phenylene-diamine-4,6-disulphonic acid	greenish yellow
403	— do —	1-ethyl-4-methyl-6-hydroxypyrid-2-one	cyanuric chloride	ethylene diamine	— do —
404	— do —	— do —	2,4-dichloro-6-(2'-methyl-5'-sulphoamino)- <i>s</i> -triazine	hydrazine	— do —
405	— do —	— do —	— do —	N-methylhydrazine	— do —
406	— do —	— do —	2,4-dichloro-6-methoxy- <i>s</i> -triazine	1,4-phenylene-diamine-2,5-disulphonic acid	— do —
407	— do —	— do —	2,4-dichloro-6-amino- <i>s</i> -triazine	1,3-phenylene-diamine-4-sulphonic acid	— do —
408	1,3-phenylene-diamine-4,6-disulphonic acid	4-methyl-2,6-dihydroxy-pyridine	2,4-dichloro-6-(4'-sulpho(4'-sulphophenoxy)- <i>s</i> -triazine	1,4-phenylene-diamine-2,5-disulphonic acid	greenish yellow

Example	II	III	IV	V
410	1,3-phenylene-diamine-4,6-disulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxy-pyrid-2-one	1,4-phenylene-diamine-2-sulphonic acid	ammonia
411	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	— do —
412	— do —	— do —	1,3-phenylene-diamine-4,6-disulphonic acid	ethylamine
413	— do —	1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	ammonia
414	— do —	— do —	1,4-phenylene-diamine-2-sulphonic acid	ethanolamine
415	— do —	— do —	1,4-phenylene-diamine-2,5-disulphonic acid	ammonia
416	— do —	— do —	1,3-phenylene-diamine-4,6-disulphonic acid	— do —
417	— do —	1-ethyl-3-(diethylamino carbonyl)-4-methyl-6-hydroxypyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	— do —
418	— do —	1-ethyl-4-methyl-2,6-dihydroxypyridine	— do —	— do —
419	1,3-phenylene-diamine-4-sulphonic acid	1-ethyl-3-aminocarbonyl-4-methyl-6-hydroxypyrid-2-one	1,4-phenylene-diamine-2,5-disulphonic acid	— do —
420	— do —	1-(3'-methoxypropyl)-3-amino-carbonyl-6-hydroxy-pyrid-2-one	1,3-phenylene-diamine-4-sulphonic acid	ethanolamine

EXAMPLE 409

The process of Example 362 is repeated up to the end of the second condensation with cyanuric chloride. Then, instead of isolating the dyestuff, 18 parts of ammonia liquor (s.g. 0.88) are added, and the mixture is heated to 30°C. and stirred at 30–40°C. for 30 minutes. The pH is then adjusted to 6.5 with hydrochloric acid (36° Tw) and the dyestuff is precipitated by the addition of 15% w/v. sodium chloride. The precipitate is filtered off, washed with a 10% solution of sodium chloride and dried in vacuo at 40°C. Upon analysis it is found to contain 1.95 moles of chlorine per mole of dyestuff. It yields bright greenish-yellow shades when applied to cellulose having good fastness to washing and light.

Further examples, similar in shade to that obtained in Example 409 are obtained by condensing one mole of the diamine of column II with one mole of cyanuric chloride, diazotizing the product and coupling with one mole of the coupling component named in column III, the product being then reacted successively with one mole of the diamine of column IV one mole of cyanuric chloride and one mole of the compound in column V.

EXAMPLE 421

A solution of 13.4 parts of 1,3-phenylenediamine-4,6-disulphonic acid in 100 parts of water at 0–5°C., pH 5.0 is added rapidly to a stirred suspension prepared by adding a solution of 9.25 parts of cyanuric chloride in 30 parts of acetone to a mixture of 60 parts of water and 60 parts of ice. The mixture is stirred at 0–5°C. for 2 hours whilst the pH is maintained at 4–5 by the gradual addition of 2N sodium carbonate solution.

To the solution is then added 15 parts of hydrochloric acid solution (S.G. 1.18) and the mixture diazotised by the addition of a solution of 3.45 parts of sodium nitrite in 25 parts of water. The dichloro-triazinyl intermediate is then coupled to 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone in similar manner to Example 1.

To the reaction solution is added a neutral solution of 31.75 parts of the trisodium salt of 1-amino-4-(4'-aminoanilino)anthraquinone-2,3',5'-trisulphonic acid in 300 parts of water. The reaction mixture is then stirred and heated at 55–60°C. for 6 hours whilst the pH of the reaction mixture is maintained at 6–7 by the gradual addition of 2N sodium carbonate solution. 190 Parts of sodium chloride are added and the mixture is stirred and allowed to cool to room temperature. The precipitated dyestuff is filtered washed on the filter with 200 parts of 25% w/v sodium chloride solution and is finally dried in vacuo at 25°C.

The product was found on analysis to contain 0.95 atoms of hydrolysable chlorine per molecule of dyestuff and when applied to cellulosic textiles in conjunction with an acid binding agent yielded strong green shades fast to light and wet treatments.

EXAMPLE 422

A solution of 13.4 parts of 1,4-phenylene-diamine-2,5-disulphonic acid in 100 parts of water at 0–5°C. and pH 5.0 is added rapidly to a stirred suspension of 9.25 parts of cyanuric chloride in 30 parts of acetone and 120 parts of ice water. The mixture is stirred at 0–5°C. for 2 hours whilst the pH is maintained at 4–5 by the gradual addition of 2N sodium carbonate solution. To the solution is then added 15 parts of hydrochloric acid solution (SG.1.18) and the mixture diazotised by the addition of a solution of 3.45 parts of sodium nitrite in 25 parts of water. The dichloro-s-triazinyl intermediate is then coupled to 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone in similar manner to Example 1.

To the reaction solution is added a neutral solution of the disodium salt of 26.6 parts of 1-amino-4-(3'-amino-anilino)anthraquinone-2,4'-disulphonic acid in 250 parts of water. The reaction mixture is then heated and stirred at 55–60°C. for 7 hours whilst the pH is maintained at 6–7 by the gradual addition of 2N sodium carbonate solution. 200 Parts of sodium chloride are added and the solution is stirred and allowed to cool to room temperature. The precipitated dyestuff is filtered washed on the filter with a solution of 60 parts of sodium chloride in 200 parts of water and is finally dried in vacuo at 20°C.

The resultant dyestuff is found on analysis to contain 0.9 atoms of hydrolysable chlorine per molecule of dyestuff and when applied to cellulosic textiles in conjunction with an acid-binding agent yields olive shades fast to light and wet treatments.

EXAMPLE 423

A solution of 13.4 parts of 1,3-phenylenediamine-4,6-disulphonic acid in 100 parts of water at 0–5°C., pH 5.0 is added rapidly to a stirred suspension prepared

- by adding a solution of 9.25 parts of cyanuric chloride in 30 parts of acetone to 120 parts of ice water. The mixture is stirred at 0—5°C. for 2 hours whilst the pH is maintained at 4—5 by the gradual addition of 2N sodium carbonate solution. To the solution is then added 15 parts of hydrochloric acid solution (S.G. 1.18) and the mixture is diazotised by the addition of a solution 3.45 parts of sodium nitrite in 25 parts of water. The dichloro-*s*-triazinyl intermediate is then coupled to 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone in similar manner to Example 1.
- The resultant greenish yellow solution is stirred and a neutral solution of 9.4 parts of 1,4-phenylenediamine-2-sulphonic acid in 100 parts of water is added. The mixture is stirred at 35—40°C. for 2 hours whilst the pH is maintained at 6—7 by the gradual addition of 2N sodium carbonate solution.
- To the resultant solution is added a screened solution of the dyestuff prepared by the addition of a solution of 31.7 parts of the trisodium salt of 1-amino-3-(4'-aminoanilino)anthraquinone-2,3',5-trisulphonic acid in 250 parts of water to a stirred suspension of 9.25 parts of cyanuric chloride in 50 parts of acetone and 100 parts of water at 0—5°C. the mixture is stirred for 30 minutes whilst the pH is maintained at 4—5 by the gradual addition of 2N sodium carbonate. The reaction mixture is stirred and heated at 55—60°C. for 5 hours whilst the pH is maintained at 6—7 by the gradual addition of 2N sodium carbonate. 250 Parts of sodium chloride are added and the mixture is stirred and allowed to cool to room temperature.
- The precipitated dyestuff is filtered, washed on the filter with a solution of 60 parts of sodium chloride in 200 parts of water and is finally dried in vacuo at 25°C. The product is found on analysis to contain 2 atoms of hydrolysable chlorine per molecule of dyestuff and when applied to cellulosic fibres in conjunction with an acid-binding agent yields strong green shades fast to light and wet treatments.
- By substitution of equimolar amounts of the compounds listed in Column II for the 1,3-phenylenediamine-4,6-disulphonic acid used in the above example, equimolar amounts of the compounds listed in Column III for the 1,4-phenylenediamine-2-sulphonic acid and equimolar amounts of the compounds listed in Column IV for the dichloro-*s*-triazinyl derivative of 1-amino-4(4'-aminoanilino)anthraquinone-2,3',5-trisulphonic acid used in the above example, a series of green-olive dyestuffs of similar properties are obtained.

I Example No.	II	III	IV 2,4-dichlorotriazinyl derivative of
424	1,4-phenylenediamine-2,5-disulphonic acid	1,4-phenylene-diamine-2-sulphonic acid	1-amino-4-(3'-amino-anilino)-anthraquinone-2,4'-disulphonic acid
425	1,4-phenylenediamine-2,5-disulphonic acid	1,3-phenylenediamine-4-sulphonic acid	1-amino-4-(4'-methyl-aminoanilino)-anthraquinone-2,3'-disulphonic acid
426	1,3-phenylenediamine-4,6-disulphonic acid	ditto	1-amino-4-(2',4',6'-trimethyl-3'-amino-anilino) anthraquinone-2,3'-disulphonic acid
427	Ditto	1,4-phenylenediamine-2-sulphonic acid	1-amino-4-(4'-aminoanilino)anthraquinone-2,3'-disulphonic acid
428	1,4-phenylenediamine-2,5-disulphonic acid	4-amino-N-methylaniline-2-sulphonic acid	1-amino-4-(4'-aminodiphenylamino)anthraquinone-2,2',3'-trisulphonic acid

EXAMPLE 429

A mixture of 11.7 parts of 6-nitro-2-aminophenol-4-sulphonic acid, 150 parts of water and 15 parts of hydrochloric acid (36°Tw) is stirred at 0—5°C. and 2N sodium nitrite solution is added until a faint excess of nitrous acid persists. The excess of nitrous acid is removed by addition of 10% aqueous solution of sulphamic acid and the resultant suspension is added to a solution prepared by adding sodium hydroxide (40%) to a suspension of 12.05 parts of 1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one in 150 parts of water until solution is just complete and then adding 20 parts of crystalline sodium acetate.

The mixture is stirred at 5—10°C. for 5 hours and the precipitate is collected by filtration and washed with a 5% aqueous solution of sodium chloride.

A mixture of the monoazo compound so obtained, 12 parts of chromium acetate and 150 parts of water is stirred and refluxed for 1 hour when formation of the 1:2-chromium complex is complete. The solution is cooled to 10° and the complex is precipitated by the addition of sodium chloride and is filtered and washed with an ice-cold 10% aqueous solution of sodium chloride before being dried at 40°.

To a suspension prepared by adding a solution of 5.0 parts of cyanuric chloride in 30 parts of acetone to a mixture of 50 parts of ice and 50 parts of water is added a solution of 6.06 parts of the 1:2-chromium complex prepared as described above in 150 parts of water at 5°C. and pH 6.5 and the mixture is stirred at 0—5°C. for

5

10

15

20

1 hour, the pH being maintained at 6—7 by means of addition of sodium carbonate as required. To the resulting solution is added a solution of 4.34 parts of aniline-3-sulphonic acid in 100 parts of water at pH 6.5, and the mixture is stirred at 30° for 1 hour, the pH being maintained at 6—7 by means of the addition of sodium carbonate as required.

The solution is cooled to 10°C. and the dyestuff precipitated by the addition of sodium chloride, collected by filtration, and dried in vacuo at 40°C. On analysis, the dyestuff is found to contain 2.2 mols of hydrolysable chlorine per mol. of the dye.

When applied to cellulose the dye gives red shades fast to washing and light.

EXAMPLE 430

A solution of 23.4 parts of 2-amino-6-nitrophenol-4-sulphonic acid in 450 parts of water containing 50 parts of 2N aqueous sodium nitrite is added to 150 parts of 2N hydrochloric acid at 0—4°C. to give a yellow diazonium salt solution. This is added to a neutral solution of 17.8 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyridine-2-one in 500 parts of water and pH raised slowly to 7.5 by the addition of 2N sodium hydroxide. The yellow azo dyestuff is then reacted with 20 parts of chromium acetate at pH 5.5—6.0 by heating at 95°—100°C. for 1 hour. The red solution of 2:1-chromium complex is filtered and treated with 40 parts of sodium sulphide crystals added portionwise over 1 hour at 90°C./pH 7—8. The mixture is filtered, cooled acidified with 50 parts of concentrated hydrochloric acid to Congo Red at the 2:1-chromium complex isolated by the addition of salt, filtration and washing with a little acetone.

16.1 Parts of the above 2:1-chromium complex is reacted with 7.4 parts cyanuric chloride at 0—5°C./pH 5—6 and 7.0 parts of metanilic acid at 30—40°C./pH 5.0—6.5 to give a dyestuff dyeing and printing cotton and viscose rayon in brick-red shades having excellent fastness to washing and light.

EXAMPLE 431

In place of 23.4 parts of 2-amino-6-nitrophenol-4-sulphonic acid used in Example 430 there are used 23.4 parts of 2-amino-4-nitrophenol-6-sulphonic acid whereby a similar dyestuff is obtained.

EXAMPLE 432

In place of 7.0 parts of metanilic acid used in Example 430 there are used 8 parts of 0.88 ammonia at 30—40°/pH 8.5—9.0 whereby a similar dyestuff is obtained.

EXAMPLE 433

A solution of 13.4 parts of 1:4-phenylenediamine-2:5-disulphonic acid in 100 parts of water at 0—5° and pH 5.0 is added rapidly to a stirred suspension prepared by adding a solution of 0.25 parts of cyanuric chloride in 30 parts of acetone to a mixture of 60 parts of water and 60 parts of ice. The mixture is stirred at 0—5°C. for 2 hours maintaining pH at 4—5 with 2N sodium carbonate solution as required.

To the solution is added 15 parts of hydrochloric acid (36°Tw) and the mixture is diazotised by addition of 3.45 parts of sodium nitrite dissolved in 25 parts of water. The dichloro-s-triazinyl intermediate is then coupled to 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone in similar manner to Example 1.

28.8 Parts of copper phthalocyanine is converted to sulphonchloride by heating with 250 parts of chlorosulphonic acid at 135—140°C. for 4 hours. The reaction mixture is drained on ice, and the precipitated sulphonchloride filtered off, washed with ice-water and drained well. The sulphonchloride is suspended in water, a solution of 14.7 parts of the sodium salt of 1:4-phenylenediamine-3-sulphonic acid added, followed by 33.6 parts of sodium bicarbonate. The mixture is stirred at room temperature for 18 hours, when the product is precipitated by the addition of concentrated hydrochloric acid, filtered off, washed with dilute hydrochloric acid solution and dried. It is then dissolved in 500 parts of water by adding 2N sodium hydroxide solution until the pH is 7. The dichlorotriazinyl derivative described in paragraph two above is added and the temperature is raised to 60°C. and the pH of the mixture is kept at 6 by the addition of 2N sodium carbonate solution until the reaction is complete. The product is precipitated by the addition of salt, filtered off and dried. It dyes cotton a dull green shade.

EXAMPLE 434

A solution of 13.4 parts of 1:3-phenylenediamine-4:6-disulphonic acid in 100 parts of water at 0—5°C. and pH 5.0 is added rapidly to a stirred suspension prepared

by adding a solution of 9.25 parts of cyanuric chloride in 30 parts of acetone to a mixture of 60 parts of water and 60 parts of ice. The mixture is stirred at 0—5°C. for 2 hours maintaining pH at 4—5 with 2N sodium carbonate solution as required.

To the solution is added 15 parts of hydrochloric acid (36°Tw) and the mixture is diazotised by addition of 3.45 parts of sodium nitrite dissolved in 25 parts of water. The dichloro-*s*-triazinyl intermediate is then coupled to 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone in similar manner to Example 1.

28.8 Parts of copper phthalocyanine is converted to sulphonchloride by heating with 250 parts of chlorsulphonic acid at 135—140°C. for 4 hours. The reaction mixture is drained on ice, and the precipitated sulphonchloride filtered off, washed with ice-water and drained well. The sulphonchloride is suspended in water, a solution of 14.7 parts of the sodium salt of 1:4-phenylenediamine-3-sulphonic acid added, followed by 33.6 parts of sodium bicarbonate. The mixture is stirred at room temperature for 18 hours, when the product is precipitated by the addition of concentrated hydrochloric acid, filtered off, washed with dilute hydrochloric acid solution and dried. It is then dissolved in 500 parts of water by adding 2N sodium hydroxide solution until the pH is 7. The solution is cooled to 5°C. and a solution of 9.25 parts of cyanuric chloride in 60 parts of acetone is added. The pH of the mixture is left at 6 by adding 50 parts of N sodium hydroxide solution as required. A solution of 10.5 parts of the sodium salt of 1:4-phenylenediamine-3-sulphonic acid is added, the temperature is raised to 35—40°C. and the pH is left at 6 by the addition of 50 parts of N sodium hydroxide as required. The dichlorotriazinyl derivative of paragraph two above is added, and the temperature is raised to 60°C. and the pH of the mixture is left at 6 by the addition of 2N sodium carbonate solution until the reaction is complete. The product is precipitated by the addition of salt, filtered off and dried. It dyes cotton a bright green shade.

EXAMPLE 435

A mixture of 19.15 parts of 2-naphthylamine-3,6,8-trisulphonic acid, 250 parts of water and 15 parts of hydrochloric acid (36°Tw) is stirred at 0—5°C. and 2N sodium nitrite solution is added until a faint excess of nitrous acid persists. The excess nitrous acid is removed by addition of 10% aqueous solution of sulphamic acid and the resulting suspension is added to a solution prepared by adding sodium hydroxide solution (40%) to a suspension of 12.1 parts of 1-(3'-aminophenyl)-3-cyano-4-methyl-6-hydroxypyrid-2-one in 150 parts of water until solution is just complete and then adding glacial acetic acid until the pH of the solution is 5.

The mixture is stirred at 10° for 4 hours and the precipitate is filtered, washed with a 10% aqueous solution of sodium chloride, and dried in vacuo at 40°.

A solution of 12.7 parts of the monoazo component in 150 parts of water at 0—5°C. and pH 6.5 is rapidly added to a suspension prepared by adding a solution of 4.0 parts of cyanuric chloride in 20 parts of acetone to a mixture of 50 parts of ice and 50 parts of water. The solution is stirred at 0—5°C. for 1 hour, the pH being maintained between 6 and 7 by the addition of 2N sodium carbonate as required.

A solution of 4 parts of 4,4'-diaminodiphenylurea-2,2'-disulphonic acid in 50 parts of water at pH 7 is added and the mixture is stirred at 35° for 2 hours maintaining the pH at 6—7 by the addition of sodium carbonate as required. The product obtained by precipitation with potassium chloride is a disazo dyestuff which gives yellow shades on cellulose fast to washing and light.

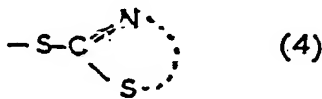
EXAMPLES 436—438

Replacement of the 4,4'-diamino-diphenylurea-2,2'-disulphonic acid used in Example 435 with an equivalent quantity of (Example 436) 4,4'-diaminostilbene-2,2'-disulphonic acid, (Example 437) 4,4'-diaminodiphenoxyethane-2,2'-disulphonic acid, or (Example 438) benzidine-2,2'-disulphonic acid yields disazo dyestuffs fast to washing and light.

The invention also provides a process for manufacture of the azo dyestuffs of the invention which contain as the reactive group one or more 1:3:5-triazine or pyrimidine nuclei substituted by a quaternary ammonium group or one or more —SO₃H,



or



groups, as previously defined herein, by reacting the corresponding dyestuff containing one or more chlorine or bromine atoms attached to the 1:3:5-triazine or pyrimidine nuclei with a tertiary amine, e.g. trimethylamine and pyridine, an alkali metal sulphite, an alkali metal salt of a dithiocarbamate e.g. sodium dimethyl-, diethyl-, diphenyl- or pentamethylene-dithiocarbamate or an alkali metal salt of a 2-mercaptobenzthiazole e.g. 2-mercaptobenzthiazole, 2-mercapto-6-methoxybenzthiazole or 2-mercapto-6-methylbenzthiazole or 2-mercapto-6-sulphobenzthiazole.

This process can conveniently be carried out by stirring a mixture of the dyestuff and the co-reactant in aqueous solution at a temperature, as appropriate, from 20 to 80°C. followed by isolation in a conventional manner, e.g. by spray-drying the reaction mixture in which the dyestuff has been formed, or by precipitation by salting followed by filtration of the precipitated dyestuff.

This process is illustrated by the following Examples in which parts are by weight:—

EXAMPLE 439

A solution of 7.4 parts of cyanuric chloride in 50 parts of acetone is added with stirring to 100 parts of water at 0° to 4°C. A solution of the sodium salt of 7.52 parts of 1:3-diaminobenzene-4-sulphonic acid in 120 parts of water is then added, the temperature of the mixture being maintained at 0° to 4°C. by external cooling. After the reaction is complete the pH of the mixture is raised to between 6.5 and 7 by the addition of sodium carbonate and a solution of the sodium salt of 6.93 parts of metanilic acid in 100 parts of water is added. The mixture is then stirred for 4 hours at 30° to 40° while the pH of the mixture is maintained between 4.5 and 6 by the addition of sodium carbonate. The resulting solution is cooled to 0°C., 20 parts of a 2N aqueous solution of sodium nitrite are added, followed by 12 parts of a concentrated aqueous solution of hydrochloric acid. The mixture is stirred for 30 minutes and the excess nitrous acid is then destroyed by addition of sulphamic acid. The resulting mixture containing the diazo compound is added with stirring to a slightly alkaline solution of 7.3 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in 200 parts of water at 0° to 4°C., and the pH is adjusted to between 7.5 and 8.0. After coupling is completed, acetic acid is added to lower the pH to 6.0, the temperature is raised to 20°C., and the dyestuff precipitated by the addition of sodium chloride. The precipitate is then filtered off and redissolved in 500 parts of water at 20°C. with stirring. A solution of 7 parts of trimethylamine in 20 parts of water is then added and the mixture is stirred for 30 minutes. The pH of the mixture is then adjusted to 7.0 by the dropwise addition of hydrochloric acid (36° Tw) and the dyestuff is precipitated by addition of sodium chloride. The precipitate is filtered off and dried at 20°C.

When applied to cotton and viscose rayon textile materials in conjunction with a treatment with an acid-binding agent the dyestuff yields bright greenish-yellow shades having excellent fastness to wet treatments such as washing and to light.

EXAMPLE 440

A solution of 13.4 parts of 1,4-phenylenediamine-2,5-disulphonic acid in 150 parts of water is added to a suspension of 9.25 parts of cyanuric chloride in 100 parts of water and 30 parts of acetone at 0—5°C. The mixture is stirred at 0—5°C. for 2 hours maintaining the pH at 6—7 by addition of 2N sodium carbonate solution as required. The solution is then acidified by the addition of 10 parts of hydrochloric acid solution (36° Tw) and 3.45 parts of sodium nitrite dissolved in 25 parts of water is added. The excess of nitrous acid is removed by addition of sulphamic acid and the mixture is added to a solution of 8.9 parts of 1-ethyl-3-cyano-4-methyl-6-hydroxypyrid-2-one in 150 parts of water at 5—10°C. and pH 6.5. The mixture is stirred at 5—10°C. for 4 hours, maintaining the pH at 6—7 by addition of 2N sodium carbonate solution as required.

The solution is then warmed to 20—25°C., a solution of 10.6 parts of the sodium salt of 2-mercaptobenzthiazole in 100 parts of water is added and the mixture is stirred at 30°C. for 4 hours. The dyestuff is then precipitated by addition of sodium chloride, filtered and dried.

When applied to cellulose it gives reddish-yellow shades which are fast to washing and to light.

EXAMPLE 441

In place of the 10.6 parts of 2-mercaptobenzthiazole used in Example 440 there are used 8.6 parts of sodium diethyldithiocarbamate when a dyestuff similar in shade is obtained and which has good fastness to washing and to light.

EXAMPLE 442

In place of the 10.6 parts of 2-mercaptobenzthiazole used in Example 440, there are used 17.2 parts of sodium diethyldithiocarbamate. The resultant dyestuff also gives reddish-yellow shades when applied to cellulose.

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EXAMPLE 443

In place of the 10.6 parts of 2-mercaptobenzthiazole used in Example 440 there is added 10.05 parts of 4,4'-diaminodiphenylurea-2,2'-disulphonic acid dissolved in 100 parts of water at pH 6.5. The solution is then stirred at 35—40°C. for 5 hours maintaining the pH at 6—7 with 2N sodium carbonate solution as required.

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To the solution there are then added 5 parts of pyridine and 7.5 parts of sodium sulphite and the mixture is stirred at 60°C. until sulphiting is complete, as judged by estimation of liberated sodium chloride. The dyestuff is precipitated by addition of potassium chloride and dried. When applied to cellulose it gives reddish yellow shades which have good fastness to washing and to light.

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EXAMPLE 444

In place of the 10.05 parts of 4,4'-diaminodiphenylurea-2,2'-disulphonic acid used in Example 443 there are used 10.1 parts of 4,4'-diaminodiphenoxyethane-2,2'-disulphonic acid when a dyestuff similar in shade with good fastness to washing and to light is obtained.

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EXAMPLE 445 and 446

To a solution of the dyestuff obtained as described in Example 292, before isolation with sodium chloride, there are added 3 parts of pyridine and 2 parts of sodium sulphite. The solution is then stirred at 60°C. until sulphiting is complete, as judged by estimation of liberated sodium chloride. The dyestuff is precipitated by addition of potassium chloride and dried. When applied to cellulose it gives bright bluish red shades with good fastness to washing and to light.

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The corresponding 1:2 cobalt complex (Example 446) gives orange shades when applied to cellulose with good fastness to washing and to light.

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The new reactive azo dyestuffs of the invention are particularly valuable for colouring cellulose textile materials, to which they are applied by dyeing, padding or printing processes in conjunction with a treatment with an alkaline agent. The dyestuffs have excellent build-up properties and the resulting colourations have excellent fastness to light and to the wet treatments which are commonly applied to cellulose textile materials.

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WHAT WE CLAIM IS:—

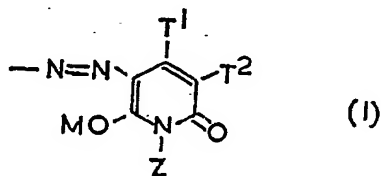
1. Water-soluble dyestuffs containing a sufficient number of sulphonic acid groups to provide water-solubility, one or more cellulose-reactive groups and at least one 3-azo-2-hydroxy-6-pyridone radical.

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2. Water-soluble dyestuffs containing at least one sulphonic acid group, at least one cellulose-reactive group and at least one group of the formula:

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wherein Z represents a hydrogen atom or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted,

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T¹ represents a hydrogen atom, a CN, COOR¹, CONR¹R², COR¹ or OH group or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted, and R¹ and R² each independently represents a hydrogen atom, an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted or the group —NR¹R² represents the radical of a 5- or 6-membered heterocyclic ring compound,

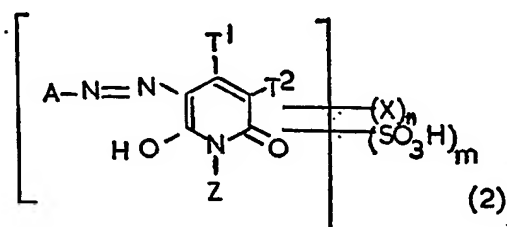
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T² represents a hydrogen atom, a CN, COOR¹, CONR¹R², or COR¹ group or an alkyl, aralkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted, and M represents a hydrogen atom or a metal atom forming part of a metal-complex system in the dyestuff.

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3. Monoazo dyestuffs of the formula:



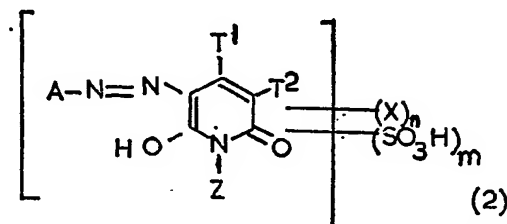
wherein A represents a benzene or naphthalene nucleus,

X is a fibre-reactive group;

Z, T¹ and T² have the meanings stated in Claim 2,

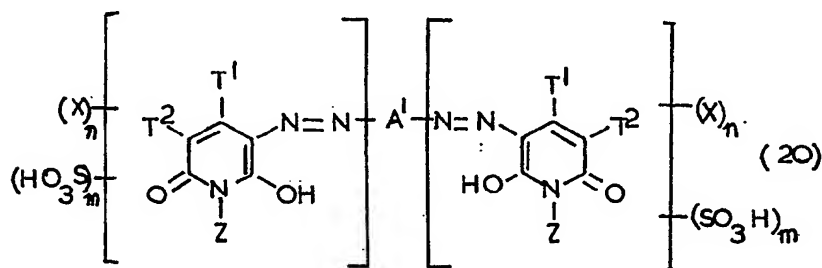
n is a positive integer of at least 1; and m is a positive integer of at least 1.

4. Disazo dyestuffs of the formula:



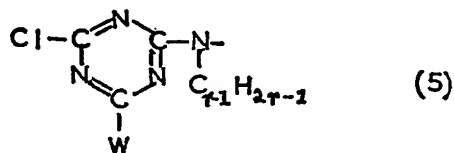
wherein A represents a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series, and T¹, T², X, Z, m and n have the meanings stated in Claim 3.

5. Disazo dyestuffs of the formula:



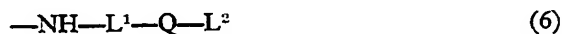
wherein T¹, T², X, Z, m and n have the meanings stated in Claim 3 and A¹ represents an aromatic radical comprising two benzene or naphthalene nuclei linked together by a direct link or a bridging atom or group.

6. A dyestuff as claimed in any preceding claim wherein the fibre-reactive group is a group of the formula:



wherein r is 1 or 2 and W is a chlorine atom, an optionally substituted amino group or an etherified hydroxyl group.

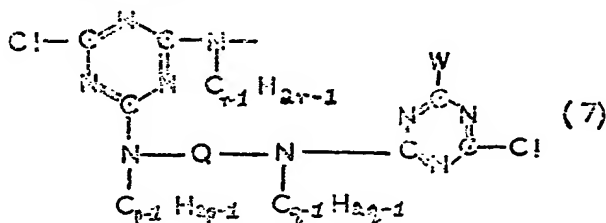
7. A dyestuff as claimed in any of Claims 1 to 5 wherein the fibre-reactive group is represented by the general formula:



wherein L¹ is a pyrimidine or triazine ring optionally carrying a labile substituent, L²

is a pyrimidine or triazine ring carrying at least one labile substituent and Q is a bridging member which is linked to L¹ and L² through optionally substituted amino groups, said imino groups being linked together through an alkylene or arylene radical.

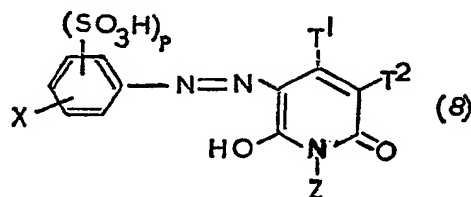
8. A dyestuff as claimed in any of claims 1 to 5 wherein the fibre-reactive group is represented by the general formula:



wherein p, q and r are each independently 1 or 2 and W and Q have the meanings stated in claims 6 and 7 respectively.

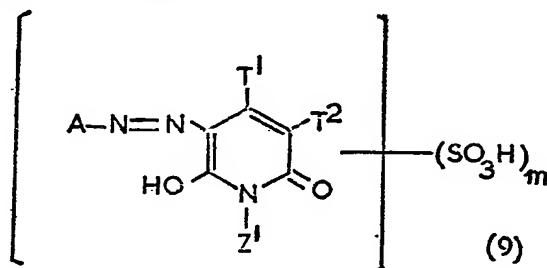
9. A dyestuff as claimed in Claim 6 or Claim 8 in which the group represented by the symbol W is a group containing a chromophonic system linked to the carbon atom of the triazine ring through —NH— or —O—.

10. A dyestuff of the formula:



- wherein T¹, T², X and Z have the meanings stated in Claims 2 and 3, the fibre-reactive group represented by X being attached to the benzene ring in *m*- or *p*-position to the azo group, and *p* is 1 or 2.

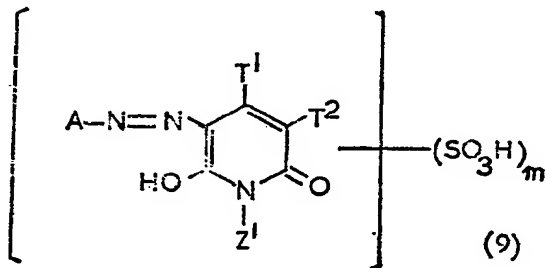
11. A dyestuff of the formula:



- wherein A represents a benzene or naphthalene nucleus or a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series, Z¹ represents an aliphatic radical containing a nitrogen atom to which is attached a cellulose-reactive group, *m* is a positive integer and T¹ and T² have the meanings stated in Claim 2.

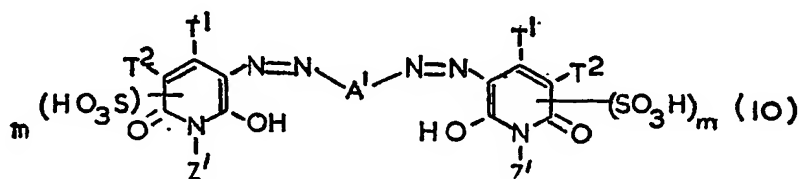
12. A dyestuff as claimed in Claim 11 wherein Z¹ represents an alkylene radical of 2 to 6 carbon atoms carrying an amino group on the α -carbon atom which amino group in turn carries the cellulose-reactive group.

13. A dyestuff of the formula:



wherein A represents a benzene or naphthalene nucleus or a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series, Z' represents a benzene radical containing a cellulose reactive group attached through an amino group to the benzene nucleus and which may be further substituted, *m* is a positive integer and T¹ and T² have the meanings stated in Claim 2.

14. A dyestuff of the formula:

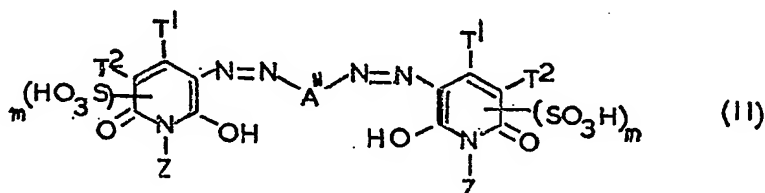


wherein T¹ and T² have the meanings stated in Claim 2,

Z' has one of the meanings stated in Claims 11, 12 and 13,

m is a positive integer, and A' represents a divalent aromatic radical.

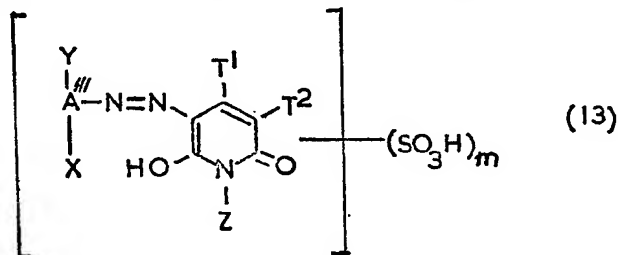
15. A dyestuff of the formula:



wherein Z, T¹ and T² have the meanings stated in Claim 2,

m is a positive integer and A'' represents a divalent aromatic radical which contains at least one fibre-reactive group.

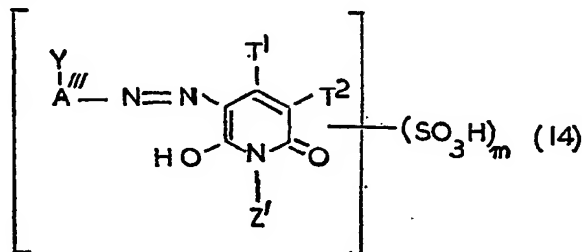
16. 1:1-copper and nickel complexes of monoazo compounds of the formula:



wherein Y stands for a hydroxyl or carboxylic acid group,

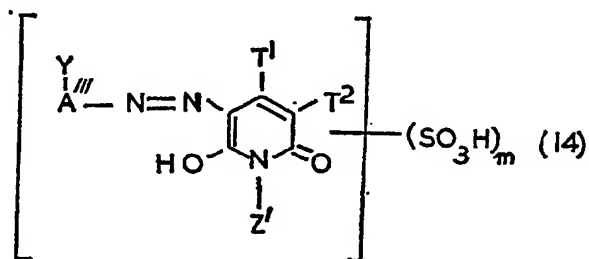
A''' stands for a benzene or naphthalene nucleus having Y ortho to the azo group, X represents a fibre-reactive group, *m* is a positive integer and T¹, T² and Z have the meanings stated in Claim 2.

17. 1:1-copper and nickel complexes and 1:2-chromium and cobalt complexes of monoazo compounds of the formula:



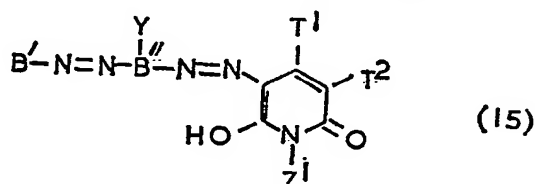
wherein *m* is a positive integer, T¹ and T² have the meanings stated in Claim 2, Z' has one of the meanings stated in Claims 11 and 12 and Y and A''' have the meanings stated in Claim 16.

18. 1:1-copper and nickel and 1:2-chromium and cobalt complexes of monoazo compounds of the formula:



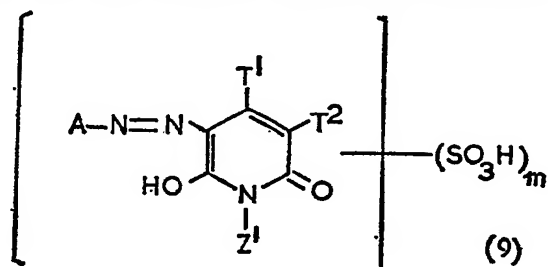
wherein m is a positive integer, T^1 and T^2 have the meanings stated in Claim 2, Z^1 has the meaning stated in Claim 13 and Y and A''' have the meanings stated in Claim 16.

19. 1:1-copper and nickel complex of disazo compounds of the formula:



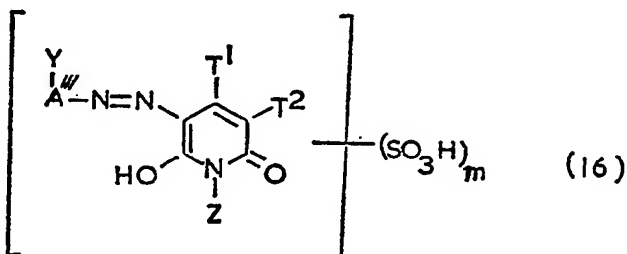
in which B' represents a benzene or naphthalene nucleus containing at least one and preferably more than one SO_3H group, B'' represents a 1,4-phenylene nucleus which may also be substituted by CH_3 or CH_3O , T^1 and T^2 have the meanings stated in Claim 2, Z^1 has one of the meanings stated in Claims 11, 12 and 13, and Y has the meaning stated in Claim 16.

20. 1:1-copper complexes of disazo compounds of the formula:



wherein m is a positive integer, T^1 and T^2 have the meanings stated in Claim 2, Z^1 has one of the meanings stated in Claims 11 and 12 and A represents an azobenzene radical in which the benzene nucleus adjacent to the pyridone nucleus carries a o -hydroxyl group and optionally a methyl or methoxy group whilst the other benzene nucleus is substituted by one or two sulphonic acid groups.

21. Cobalt or chromium complexes containing 1 mole of a monoazo compound of the formula:



wherein Z , T^1 and T^2 have the meanings stated in Claim 2, m is a positive integer, and A''' and Y have the meanings stated in Claim 16, and one mole of a polydentate

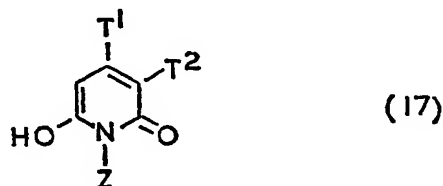
ligand containing a cellulose-reactive group linked to the Cr or Co atom.

22. A water-soluble dyestuff as claimed in Claim 1 and hereinbefore particularly described in Example 1.

5 23. A water-soluble dyestuff as claimed in Claim 1 and hereinbefore particularly described in any of Examples 170, 238 to 251 inclusive and 288 to 310 inclusive. 5

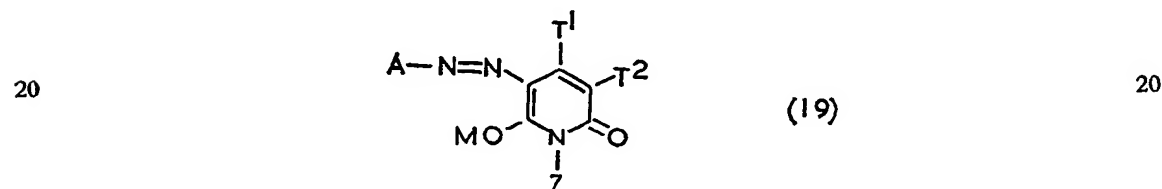
24. A water-soluble dyestuff as claimed in Claim 1 and hereinbefore particularly described in any of Examples 2 to 116 inclusive, 154 to 161 inclusive, 171 to 200 inclusive, 228 to 237 inclusive, 252 to 287 inclusive, 311 to 337 inclusive, 382 to 386 inclusive and 421 to 446 inclusive.

10 25. A process for manufacture of water-soluble dyestuffs as defined in claim 2 which comprises diazotising an aromatic amine and coupling the resulting diazo compound with a coupling component which is represented by the formula: 10



15 wherein T¹, T² and Z have the meanings stated in Claim 2, the amine and the coupling component together containing at least one fibre-reactive group and at least one sulphonic acid group. 15

26. A process for manufacture of water-soluble dyestuffs as defined in Claim 2 which contain the cellulose-reactive group or groups attached through amino groups which comprises reacting an azo dyestuff of the formula:



20 wherein A has the meaning stated for A, A', A'' or A''' in any preceding claim, T¹, T², M and Z have the meanings stated in Claim 2 and which contains an amino or alkylamino group and at least one sulphonic acid group with a reagent capable of condensing with the amino or alkylamino group and attaching thereto a residue containing a fibre-reactive group. 25

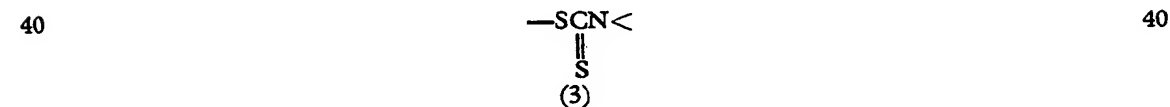
27. A process as claimed in Claim 26 wherein the reagent is carbyl sulphate.

28. A process as claimed in Claim 26 wherein the reagent is a compound of the formula:

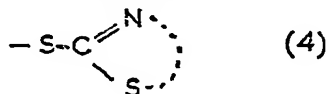
X—halogen wherein X has the meaning stated in Claim 3.

30 29. A process for manufacture of the compounds of Claim 1 which contain as the reactive group or groups one or more 1:3:5-triazine nuclei substituted by a chlorine atom and by an optionally substituted amino group by reacting the corresponding dyestuff containing at least one 1:3:5-triazine nucleus substituted by two chlorine atoms with ammonia or the appropriate primary or secondary amine under such conditions that one of the chlorine atoms attached to each 1:3:5-triazine nucleus is replaced by an optionally substituted amino group. 35

30. A process for manufacture of the compounds of Claim 1 which contain as the reactive group one or more 1,3,5-triazine or pyrimidine nuclei substituted by a quaternary ammonium group or one or more SO₃H groups,



groups wherein the nitrogen atom carries optionally substituted hydrocarbon or heterocyclic radicals, or groups of the formula:



5 wherein the dotted line represents atoms necessary to form an optionally substituted or fused heterocyclic ring, which comprises reacting the corresponding dyestuff 5 containing one or more chlorine or bromine atoms attached to the 1,3,5-triazine or pyrimidine nuclei with a tertiary amine, an alkali metal sulphite, an alkali metal salt of a dithiocarbamate or an alkali metal salt of a 2-mercaptothiazole.

10 31. A process for colouring cellulose textile materials which comprises dyeing or printing the materials with a compound as claimed in Claim 1 in conjunction with a treatment with an acid-binding agent. 10

32. Cellulose textile materials whenever coloured by a process claimed in Claim 31.

15 33. A water-soluble dyestuff as claimed in claim 1 and hereinbefore described in any of Examples 117 to 153 inclusive, 162 to 169 inclusive, 201 to 228 inclusive, 338 to 381 inclusive and 387 to 420 inclusive. 15

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